THE UNIVERSITY OF ALBERTA

AGRICULTURAL USE OF COAL-DERIVED HUMIC ACIDS

by

(C) RODNEY COLIN McKENZIE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

FALL, 1970

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Agricultural Use of Coal-Derived Humic Acids" submitted by Rodney Colin McKenzie in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Experiments were conducted with water-soluble sulfomethylated coal humic acids to determine their ability to supply nitrogen and sulphur to plants. Field and greenhouse experiments were conducted which involved barley and perennial grasses. The coal humic acids were applied to the soil in an ammoniated form and in an ammoniated form blended with urea. The efficiency of the coal humates in supplying nitrogen to barley was compared to $NaNO_3$, $(NH_4)_2SO_4$, and urea. Results showed the available nitrogen contained in the coal humates was supplied to plants, but little of the bound nitrogen was made available to plants. Coal humates did not show any appreciable slow release of nitrogen and were similar to chemical nitrogen sources in efficiency of supplying nitrogen. Sulfomethylated coal humates did serve as a sulphur supplying source for barley.

Other experiments were conducted with barley and alfalfa grown on soils which were high in soluble aluminum, to determine if coal humates could reduce the harmful effects of aluminum toxicity. Additions to the soil of coal humates reduced the amount of soluble aluminum in the soil and improved plant growth.

Experiments were conducted to determine if coal humates improved soil structure. An ammonium form of sulfomethylated coal humates improved the aggregation of soil, but the effect of this material on soil crusting was inconclusive. Ammonium and calcium forms of coal humates did not alter the hydraulic conductivity of Solonetzic soils. Ammonium and calcium forms of lignin were shown to improve the hydraulic conductivity of soil and the ammonium form of lignin was shown to increase soil aggregation. $CaCl_2$ and NH_4Cl were shown to effectively increase hydraulic conductivity of Solonetzic soils.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. M. P. K. Nyborg, Associate Professor of Soils, Department of Soil Science, under whose direction this study was undertaken. Thanks are extended to him for his assistance and encouragement with all phases of this study. His help with the gathering of data on the greenhouse experiments is also gratefully acknowledged.

Thanks are also extended to the following:

Dr. F. D. Cook, Soil Science Department, who provided helpful advice throughout the project and served on the thesis committee;

Dr. C. F. Bentley, Soil Science Department, and Dr. Z. P. Kondra, Plant Science Department, for their help and for serving on the thesis committee;

Dr. J. A. Toogood, Head of the Soil Science Department and Dr. S. Pawluk, Acting Head of the Soil Science Department, for providing the facilities for this study;

Dr. G. R. Webster, Soil Science Department, for advice and constructive criticism;

Dr. S. E. Moschopedis, Alberta Research Council, for his advice concerning the chemical properties of the coal humates and for his interest and encouragement regarding this study;

Mr. G. W. Oborn, Department of Soil Science, for his assistance with analytical work in all phases of the project;

Messrs. J. Ereiser, J. Taylor, E. Dunk, P. Nemunis-Siugzdinis, J. Likacz, and Misses S. Golinsky, and D. McLeod for efficient technical assistance;

Fellow graduate students in the Soil Science Department for advice and to D. Gould for technical assistance with analysis;

The Alberta Soil and Feed Testing Lab and the Alberta Research Council for analytical data;

Mr. A. Dezayer, Rich Valley, and Mr. J. Michael, Dunstable, who donated space for field plots and cooperated with the maintenance of these plots;

Mr. A. Ryan, Calgary, and the Alberta Agricultural Research Trust for financial sponsorship of this study; and

My wife.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF APPENDICES

INTRODUCTION

In 1957 the Research Council of Alberta initiated a coal utilization project. The purpose of the project was to develop markets for Alberta's coal deposits. To broaden the possibilities for the utilization of coal, the project began as a fundamental study of the structure of coal and coal derivatives.

Leonardite, a brown naturally oxidized coal, was one aspect of this fundamental study. A great deal of leonardite occurs in Alberta and usually ends up on the slag heaps of existing coal mines. Coal humic acids are derived from leonardite by alkali extraction and acid precipitation. Humic acids are alkali soluble, but water insoluble. Their properties do not greatly differ from soil formed humic acids.

The Research Council of Alberta developed a method of rendering these humic acids water soluble above pH 2 to 3 . This method (Moschopedis, 1965, 1967) involved replacing active hydrogen atoms (ortho or para to phenolic OH groups) within the humic acid molecule by the sulfomethyl group ($-CH_2SO_3M$). M represented a cation which was NH_4^+ in the case of most of the sulfomethylated coal humic acids (SHA) used in this study.

The sulfomethylated humic acid had considerable ability as a clay dispersant and was used as a bentonite drilling mud thinner. Despite its action as a dispersant, there was evidence that other organic dispersants, derived from wood pulp wastes (lignosulfonic acids), acted to increase soil aggregation. It was therefore believed that this material might have the ability to improve the aggregation of poorly structured soils. Poor structure is a major impediment to crop growth

in Alberta on most of the Solonetzic soils and some of the Luvisolic soils.

Considerable research work was published in Europe on the benefits obtained from humic fertilizers (Khristeva, 1963; Flaig, 1963; and many others). These researchers claimed that when coal humates and other organic additives were applied to the soil or to nutrient solutions they acted as plant growth or metabolic stimulants; increased protoplasmic permeability, thus improving uptake of nutrients; and acted as a chelating agent aiding trace element uptake. In addition, the coal humates had essential elements for plant nutrition. Coal humic acids provided a pH buffering action in nutrient solution, so it was believed they might also provide a buffering action to alleviate soil acidity damage.

The sulfomethylated humates, prepared by the Research Council, contained about 1 to 2% nitrogen derived from the coal (Flaig, 1968). The cation sites formed by sulfomethylation combined with the sites formed by carboxyl groups originally present in the humic acids, provided sites for another 2 to 3% exchangeable nitrogen which was added to the humic acid molecule. The process also increased the bound nitrogen content within the molecule. It was believed that the ammoniated sulfomethylated coal humic acid would serve as a fertilizer which would provide plants with nitrogen, as well as sulphur and iron.

At the same time, the Alberta Research Council and the Soils Department of the University of Alberta were concerned with improving efficiency of nitrogen fertilizers and reducing water pollution caused by losses of nitrogen fertilizers. If ammoniated sulfomethylated humic acid had the property of slow release of nitrogen, it would allow heavy

applications of nitrogen fertilizers, which would then release nitrogen slowly, somewhat in relation to plant needs. That would reduce the amount of free ammonia and free nitrate in the soil, subject to volatilization and leaching losses, respectively. It would also reduce seedling damage caused by an excess of ammonium ions present in the soil at germination time.

Initial small scale trials of sulfomethylated humic acids (SHA) by the Soils Department of the University of Alberta and the CDA Soil Research Substation, Vegreville, Alberta indicated the SHA might have some slow release properties. Further studies of agricultural applications of SHA were undertaken by the Soil Science and Plant Science Departments, University of Alberta, with financial support from the Alberta Agricultural Research Trust. The Soils Research Substation at Vegreville also undertook to continue testing SHA on Solonetzic soils.

The study of sulfomethylated coal humic acid, described in this thesis, was undertaken to determine if sulfomethylated humic acids:

- function as slow release nitrogen fertilizers;
- give to crops additional benefits different from inorganic fertilizers;
- serve as a sulphur fertilizer on sulphur-deficient soils;
- alleviate soil acidity damage to crops; and
- improve soil structure.

LITERATURE REVIEW

The response of plants to organic nutrients, the use of organic materials as nitrogen fertilizer carriers to provide slow release of nitrogen, and the value of organic materials as soil structural amendments are the three areas which will be discussed in the literature review. The available literature on coal humates, as well as other organic materials, will be considered.

Response of Plants to Organic Amendments

Some of the earliest farmers applied organic amendments to the soil to improve plant growth. The Romans used organic manures as recorded by Petrus Crescentius of Bologna in his agricultural treatises, first published in 1240. Russell (1961) described Palissy's statement in 1563, "dung ... is to return something which has been taken away". The Iroquois Indians planted a fish with each hill of corn.

Research work into the cause of these growth effects is relatively recent. Considerable work was done in Europe during the last century to show responses of plants to organic manure treatments. Generally, the organic manures were compared to controls consisting of either no fertilizer, or else fertilizers at rates which were not equivalent to the level of nutrients applied as organic manures. In the classic experiments of Rothamstead, conducted by Gilbert and Lawes, average yields obtained were 41.5 bushels per acre of wheat (*Triticum aestivum*) over 51 years in the manured plots and 39.6 bushels per acre over the same period in the best of the chemically fertilized plots. However, they made no attempt to equalize applications of plant nutrients in those two treatments.

More recently attempts were made to separate the various effects

of organic manures on plant growth. The interpretations of these effects fall into several categories:

- growth effects due to substances present in the organic material that act as growth stimulants;
- essential elements provided by the organic matter;
- chelation of nutrients which aids in their uptake or translocation; and
- improvement of soil structure, thus improving the potential of the soil for crop production.

The effect of organic matter on pedogenic processes is a longer term process which is beyond the scope of this study. For example, in Europe heavy applications of organic manures have resulted in Chernozem-like A_h horizons on a wide variety of soil types. An alteration of surface soil horizons results in altered growth responses of plants to that soil.

Evidence for Uptake of Organic Substances

If plants adsorb and translocate large organic molecules, the possibility of these organic molecules influencing the plants' metabolic processes is greatly increased. Führ and Sauerbeck (1963) observed the uptake of C^{14} labelled humic acid and fulvic acid into sunflowers (*Helianthus annuus*). They found that the amounts of uptake in the roots was 6% of the added fulvic acid and 27% of the added humic acid, but the uptake into the shoots was only 0.5% of the fulvic acid and 0.1% of the humic acid. The authors admitted difficulties occurred in cleaning the roots of humates which accumulated on the surface. Aso and Sakai (1963) used the color change which occurred with mulberry (*Morus*) seedlings and

petioles as indicating uptake of humates derived from coal. They achieved quite a remarkable darkening of tissue extracts from plants which were grown in a nutrient solution which contained 0.1% (by weight) coal humic acids. Guminski (1968) suggested this darkening could have been caused by an enzyme oxidation of polyphenols or endogenic amino acids. A number of workers, De Kock and Stremecki (1954), Aso and Sakai (1963), and Guminski (1968), showed that humates increased the uptake of labelled or total iron in various types of nutrient solutions. This did not necessarily indicate the translocation of the humate molecule. Kaneda and Moschopedis (1969) showed, by autoradiography, uptake of C^{14} labelled coal humates in leaf cuttings of tobacco (*Nicotiana tabacum*). However, this material was concentrated only in the midrib and main veins in the short time the experiment was conducted. From the foregoing data it appears that the evidence is inconclusive concerning the uptake of humates, fulvates, and similar large organic molecules.

Führ and Sauerbeck (1965) used C^{14} labellec humic and fulvic acid solutions on carrot (*Daucus carota*) plants grown in nutrient solutions. Radioautographs showed C^{14} accumulated on, or perhaps in, the root epidermis, but small amounts were found in the plant. Chemical analysis showed some C^{14} in the components of sugar metabolism when either fulvic or humic acids were applied. The authors thought this implied mainly low molecular weight products of the added organic matter were taken up and utilized by the plants. The high concentration of C^{14} on the roots was due to adsorbed material.

Nutritional Value of Organic Amendments in Soil Cultures

Organic matter, including coal humates, contains carbon and most

of the other elements which are required by a plant. Führ and Sauerbeck (1963) suggested organic carbon taken from the soil served to supply a portion of the plants' carbon needs. They reported a figure of 12 kg organic carbon uptake per hectare with sunflowers (Helianthus annuus). This, however, was almost totally found in the roots. Other elements present in the coal humates were Na, Mg, Al, P, Si, K, Ca, Fe, and trace amounts of 22 other elements (De Kock and Stremecki, 1954). Nitrogen was found in most coal deposits and coal humates (Flaig, 1968). When coal humates were applied to plants grown in soil, their benefits to growth could most frequently be explained by the nitrogen found in coal.

The work of Hoyt (1968) at Beaverlodge showed that barley (Hordeum vulgare), grown for several years on plots receiving one application of 60 tons farmyard manure per acre plus heavy applications of chemical macro and micro nutrients, yielded about the same as barley on plots which only received the chemical fertilizers. This agreed with the findings of Kozhekov, Lazareva, Abasova, Kulikova, and Kovaleva (1968) who grew corn (Zea mays) and sugar beets (Beta vulgaris) in field and pot experiments. They fertilized these crops with coal humates and chemical fertilizers. They attributed yield increases over unfertilized plots to nitrogen and phosphorus present in the coal humates and obtained no yield increases over comparable chemically fertilized controls.

Khristeva (1963) gave data on a large number of field experiments using peat and coal humates as fertilizers and she compared these materials to equivalent amounts of N, P, and K applied as chemical fertilizers. In most of her experiments, the organically fertilized soils showed greater plant yields than chemically fertilized soils. But there were some experiments in which plots fertilized with humates applied at great-

er than 20 tons per hectare produced smaller yields than plots fertilized with equivalent chemical applications.

Increases in yield of the organic fertilizers over the chemical fertilizers were largest on Sod Podzols, which had low organic matter and contained only a small percentage of humic acid in this organic matter. Sod Podzols treated with humates gave yields more than 50% greater than the treatment with equivalent nutrients in the form of chemical fertilizer. Khristeva (1963) suggested the best responses of plants to organic fertilizers were on Podzols, chestnut soils, and drifting sands; with little advantage on Chernozems and Grey Woodland soils. Similar positive results with organic fertilizers were expressed by Haken (1963) with manure, and by Dragunov (1963) and Niklewski (1963) with peat fertilizers.

Nutritional Value of Organic Amendments in Nutrient Solutions

Researchers have done considerable work with nutrient solutions showing positive growth responses of plants due to coal humates and other organic additives. De Kock and Stremecki (1954), Chaminade (1958), Kononova and D'Yakonova (1960), Khristeva and Luk'Yaneko (1962), Řeřábek (1963), Aso and Sakai (1963), Schnitzer and Poapst (1967), and Freeman and Fowkes (1969) conducted experiments with nutrient solutions containing coal humates, fulvic and humic acids derived from soil, plant auxins (such as indole acetic acid), or other compounds. All the preceding workers got increased growth of plants in some situations with the organic compounds that they tested.

Freeman and Fowkes (1969) showed significant plant growth responses when humates derived from coal were added to nutrient solutions.

The growth stimulation was attributed to pH stabilization of the nutrient solution by the humates preventing iron precipitation, and to chelation of iron by the humates aiding iron uptake by the plants. The idea of humates chelating iron and therefore aiding iron uptake by plants is in agreement with De Kock (1960) and Aso and Takenaga (1968). The latter workers also concluded that the chelating molecule was adsorbed by the plant roots. Freeman and Fowkes noted the humates became toxic when in excess of 1% (by weight) of solution.

A number of researchers tested organic compounds on seedlings to determine if they altered the amount of root development. Schnitzer and Poapst (1967) increased root initiations on seedlings treated with fulvic acids. Freeman and Fowkes (1969) increased root initiations with coal derived humic acids. In addition, the latter workers obtained significant increases in rates of elongations of root sections with coal humates and indole acetic acid (IAA), but only IAA increased the elongation of stem sections. From this they concluded humic acid influenced meristomatic areas, while IAA also acted upon cell elongation. Both groups of workers concluded that the organic additives played a role in making iron available to meristomatic regions and because of this, the additives increased root development.

Khristeva and Luk'Yaneko (1962) and Smidova (1962) expressed the view that organic additives relieved oxygen deficiency by serving as hydrogen acceptors. The former gave data from nutrient culture work to show this resulted in better toleration of heat, drought, and excess ammonium. The last observation was also made by Chaminade (1958). Guminski (1968), however, disagreed with the above workers and suggested that the observed beneficial effects of the humates were obtained because the

humates aided iron uptake by chelation.

Řeřábek (1963) suggested humic acids derived from coal served as detoxifying agents. When some organic substances were applied at toxic levels the coal humate formed bonds with the toxin or stimulated enzymatic activity within the plant cell and this increased activity reduced the effect of the toxins.

A number of workers, for example Prat (1963b), conducted experiments designed to show humates increased the permeability of protoplasm. This was discussed in a review by Heinrich (1964). The relation of increased protoplasmic permeability to plant growth was not established.

Other Growth Effects of Organic Substances

Another claim for humates was that they functioned as correcting agents for metabolic diseases of plants similar to the way vitamins functioned in animals (Khristeva, 1963). Whitehead (1963) suggested a number of ways in which organic compounds aided plant growth, such as releasing decomposition products that served as specific antibiotics, acting as toxins to certain fungi, and producing resistance to penetration of pathogenic fungi into plant tissue. He also suggested that predacious fungi, which feed on nematodes, could be increased by organic additions to the soil.

Interpretations

Two opposing views emerge from the literature: (i) organic amendments have little or no growth promoting effects on a plant supplied with adequate chemical nutrition; (ii) organic amendments in many cases aid in plant nutrition and increase plant growth. Russell (1961) stated, "Provided the soil conditions as regard air and water supply are favor-

able, it appears the value of farmyard manure as measured by crop yields depends only on the amount of nutrients it can supply in simple form to the crop. There is, in fact, no well established evidence that adding any vitamin or growth promoting factor to the soil ever improves crop production." In agreement with this, Hoyt (1968) found that additions of large quantities of farmyard manure had little effect on well fertilized crops on Luvisolic soils. While Khristeva (1963) got little additional plant growth response from organic fertilizers over chemical fertilizers when they were applied to Grey Wooded soils, she did get large responses from organic additives on Sierozems, Chestnut soils, and Podzols. In contrast to Khristeva's work, Kozhekov, Lazareva, Abasova, Kulikova, and Kovaleva (1968) used Sierozemic soils and did not get a plant growth response to coal humates different from chemically fertilized controls. The long time experiments at Rothamstead showed a slight yield increase for the manures, but this might be attributable to improved structure. The controversy on whether organic matter aids growth of a plant supplied with adequate chemical nutrition still exists.

Perhaps deficiencies of experimental design have contributed to the controversy regarding the benefits of organic fertilizers. Khristeva's work (1963), on Sod Podzolic and Podzol soils, and the other favorable reports for organic fertilizers all failed to assign degrees of statistical significance to the comparisons, but expressed these as percent gain over controls. They also usually gave very limited analytical data on their product and failed to mention if comparisons were based on total nutrients in humates or readily available nutrients.

It is the opinion of the author that since 1963 a shift in thinking regarding the use of organic fertilizers occurred in the USSR. It

seems the use of such fertilizers developed due to the lack of a sufficiently large chemical fertilizer industry to supply agricultural needs. In many cases the results of the organic fertilizers were compared to chemically inadequate controls. Gerasimov (1962) interpreted resolutions of the XXII Congress of the Soviet Union to soil scientists. He emphasized greater need to rely on chemical fertilizers, factual experiments, and the need to rethink old concepts without the reliance on the cult of personality. Since that time the articles published in support of organic growth amendments were much fewer and more reserved. Guminski (1968) presented more restricted claims than were presented by Prat (1963a) and Khristeva (1963). Kozhekov, Lazareva, Abasova, Kulikova, and Kovaleva (1968) presented a paper quite critical of previous claims of plant growth stimulation by organic matter. However, the two opposing views concerning the role of organic matter in plant growth are still both prevalent.

Comparative Value of Nitrogen Sources

Crop recoveries of nitrogen from fertilizers are related to the losses of nitrogen that occur within the soil, to the form of nitrogen applied, and to the form utilized by the plant. Nitrogen losses from fertilizers are directly related to the form of nitrogen fertilizer applied and to the conversions, such as nitrification, which occur in the soil. The two principal forms of nitrogen utilized by plants are NH_4^+ and NO_3^- (Viets, 1965). Other forms of nitrogen are usually converted to NH_4^+ or NO_3^- prior to uptake by plants. If crops fertilized with either NH_4 or NO_3 nitrogen, differ with regard to yield, determination of the reasons requires precise knowledge of environmental conditions (Viets, 1965). Crop recovery of added nitrogen is usually about 50% and seldom exceeds

70% (Allison, 1965). Because crop recoveries of conventional nitrogen fertilizers are not high, it would be desirable to have a slow release fertilizer which could release nitrogen at a rate similar to the crops' requirements for nitrogen, resulting in a more efficient use of fertilizer nitrogen.

Leaching Losses

Average leaching losses of applied nitrogen range from 20% to 40% of the applied fertilizers (Harmsen and Kolenbrander, 1965). Leaching losses will occur with nitrate in any soil where movement of soil water to groundwater takes place (Viets, 1965), but with ammonia, only in soils which have a low cation exchange capacity. The amount of soil microfloral immobilization may also influence leaching losses. When ammonium is applied as fertilizer, the nitrification rate of ammonium will influence the loss of soil nitrogen in the nitrate form. Nitrification occurs most rapidly in soils under moist, well aerated conditions, warm temperatures (30° to 35°C. optimum) and near neutral pH (Alexander, 1961).

Gaseous Losses

Volatilization accounts for a considerable amount of the losses of applied soil nitrogen, commonly 5 to 20% and sometimes higher (Allison, 1966). Ammonia losses occur chiefly on soils of high pH when ammonium salts, ammonia, or urea are applied on or near the surface. It may occur from a direct reaction of ammonium salts with calcareous materials and is greater if the soils are dry or of low exchange capacity.

The major cause of nitrogen losses may be denitrification, a microbiological reaction. Alexander (1961) discusses the factors which encourage denitrification. These are:

- waterlogged conditions where the amount of organic matter is high and the temperature is an optimum of 25°C. or higher;
- a high level of nitrate or nitrite in the soil; and
- the soil pH controls the rate of the reaction and the products evolved. From pH 5 to 6 N_2O and some NO are evolved, and above pH 6 chiefly N_2 is evolved.

Nitrogen volatilization losses from urea may be high because of urea's rapid conversion to ammonia, particularly on soils with a neutral or high pH.

Other Nitrogen Losses

There are a number of other ways in which nitrogen can be lost from the soil. They are:

- microbiological immobilization;
- immobilization through chemical reactions with soil organic components; and
- interlattice fixation of NH_4^+ by clay minerals.

Utilization of Nitrogen by Plants

If crop yields differ between NO_3 and NH_4 , the two most common forms of available nitrogen, the reasons have seldom been established (Viets, 1965). Some of the different effects on plants from various nitrogen sources are:

- preferential uptake or utilization of a particular form of nitrogen. This is not common, but rice (*Oryza sativa*) plants and cotton (*Gossypium hirsutum*) seedlings prefer NH_4 .
- NO_3 serves as an oxygen source on poorly aerated soils, thus aiding crop growth;
- change of pH by carriers such as $SO_4^=$ in $(NH_4)_2SO_4$, lowering

pH of alkaline soils and increasing uptake of phosphorus;

- depression of uptake of cations, particularly K^+, by NH_4^+;
- seedling damage due to placement of nitrogen fertilizers in the seed row;
- nitrite accumulation, formed from urea and NH_4^+ fertilization, acts as a toxic agent to plants; and
- urea toxicity, because of biuret contaminants or because of rapid pH increase and NH_4 accumulation, reduces plant growth.

Slow Release of Nitrogen

Slow release of nitrogen from fertilizers is desirable to reduce previously mentioned losses and prevent pollution of groundwater by seepage water containing nitrogen. Nitrification inhibitors serve to increase the efficiency of nitrogen fertilizers and reduce the frequency of application of these materials (Beaton, Hubbard and Speer, 1967). Excess nitrogen uptake by plants may produce forages toxic to livestock (Viets, 1965). A slow release fertilizer would also reduce this problem.

Structural Effects of Organic Amendments

Soil structure has long been considered important to agricultural productivity. However, improvements of soil structure are not necessarily directly related to yield increases in crops. Gussak (1961) did not get any change in yields on Sierozems due to structural improvements. Toogood (1963) did get significant improvements in crop yields with additives to soil which improved the structure. However, these were with Solonetzic soils with very poor structure.

It has long been known that additions of organic fertilizers tend

to improve soil structure. The mechanisms, which cause these structural development characteristics, are not well understood. Jacks (1963) discusses structure development and suggests that two processes are involved: (i) cementing of particles to form aggregates; and (ii) shaping and orientation of aggregates to form macrostructures. The first of these processes shall be the main concern of this report.

The effect of organic materials on soil structure probably involves aggregation of clays. Organic materials form bonds with clays by the following methods (Greenland, 1965):

coulombic attractions between - negative clay and positive organic compound;
- positive clay surface or surface ion and negative organic compound.

van der waals forces between - clay and organic compound;
- dissimilar adsorbed molecules;
- similar adsorbed molecules.

Soils with a good aggregation often have what is referred to as a crumb structure. Swaby (1950) suggests two mechanisms are involved in stabilizing crumbs. These are: (i) waterproofing such as occurs with fats and resins; (ii) other substances which serve as binding agents. Rennie, Truog, and Allen (1954) stressed the idea that the microbial gums, formed from organic material, played a major role in soil aggregation. Swaby (1950) incubated soil humus mixtures and found no increase in aggregation when the humus was pretreated with acid or various cations. Swaby's work contradicts that of Rennie, Truog, and Allen and suggests that increases in aggregation caused by organic matter is due to other factors than the products or actions of soil microbes.

Lignin sulphite liquor was used by a number of workers as a soil structural amendment and nitrogen supplying agent. Doyle and MacLean (1959) found that an ammonium salt of this material had very limited aggregation ability initially, but this increased considerably with incubation. This agreed with Alderfer and Sharp (1955), but contrasted directly with Sowden and Atkinson (1951), who obtained the aggregation effect from direct action of the lignin material. Doyle and MacLean postulated that the effect on soil aggregation by lignin sulphite liquor was shortlived because it formed aggregates from shortlived microbial decomposition products. In contradiction, Webber (1959) gave data to show significant increase in aggregation four years after application with one of two paper manufacture wastes. Gussak (1961) on the other hand, stated that lignin wastes and coal humates did not give significant changes in structure on irrigated Sierozems.

Those who stressed the importance to soil aggregation of microbial gums, such as Rennie, Truog, and Allen (1954), obtained good aggregation with much higher applications of gum than those naturally occurring in soils. They found an increase in aggregation from organic applications and concurrent gum formation. They then emphasized the role of the gums in causing aggregation, but did not stress the importance of the humus which was formed at the same time from the breakdown of the organic residues. Lignin materials, such as those in bisulphite wastes, appeared to have quite a long lasting influence on soil aggregation (Webber, 1959). This implied that the effect on soil aggregation of the long lasting humus and lignin products was more important than the transitory effect of microbial gums and other microbial products.

The literature has not satisfactorily established whether mecha-

nisms causing aggregation of organic additives are principally physical-chemical interactions or whether they are chiefly due to the microbial byproducts of breakdown of organic materials.

MATERIALS AND METHODS

Sulfomethylated Coal Humic Acids

The Alberta Research Council prepared a number of coal humic acid products from naturally oxidized brown coal obtained at the Sheerness Mine in Alberta. The brown coal from Sheerness contained about 80% alkali soluble humic material. The coal humates were extracted and purified according to the procedure outlined by Moschopedis (1965 and 1967). The material was sulfomethylated according to the process outlined by Suter, Bair, and Bordwell (1945). A sulfomethyl ($-CH_2SO_3M$) group was added to the coal humate. Usually the cation (M) added was NH_4^+ in the form of ammonium hydroxide. The raw materials utilized in the preparation of the final water soluble coal humic acids were sodium hydroxide, ammonium hydroxide, sodium sulphite, and formaldehyde. The brown coal samples were not uniform and the manufacturing process was not standardized, so variation occurred between lots. Analytical data for the lots used in this report are shown in Appendix I. Considerable work on the structure of coal humic acid was done by the Research Council (Berkowitz, Moschopedis, and Wood, 1963). On the basis of this work a structural sketch of the approximate form of a sulfomethylated humic acid molecule is shown in Appendix II.

The nitrogen contained in the coal was present in two forms: (i) NH_4^+ (plus a trace of NO_3^-) exchangeable with 1 N KCl solution; and (ii) non-extractable, bound nitrogen which was mostly present in the original coal. Amounts of the two forms of nitrogen are given in Appendix III. Sulfomethylated coal humic acid samples, PHSC 8A and PHSC 8B, were mixed with about 30% urea. This was partly a physical mixture as shown by

over half of the added urea being recovered by spectophotometric analysis according to the procedure outlined by Watt and Chrisp (1964). The remainder of the urea was present in some bound form not detectable by tests for exchangeable NH_4^+, NO_3^-, and uncombined urea. It was hoped this blend of sulfomethylated coal humic acid and urea might have some slow release properties with respect to nitrogen.

Fertilizer Experiments

A number of fertilizer experiments were conducted under field and greenhouse conditions in which coal humic acid products (Appendices I, II, and III) were compared to commercial and chemical fertilizers.

Field Plot Experiments

The sulfomethylated coal humates were tested in the field at four sites on the following soils: Rich Valley on a Grey Solonetz, Dunstable on a Gleysolic Grey Luvisol, Busby on a Dark Grey Luvisol, and Fort Saskatchewan Hospital on a sandy lawn site. The first two of these sites were seeded to Galt barley (Hordeum vulgare), the other two were grass stands. A description of plot locations and soil analyses by the Alberta Soil and Feed Testing Laboratory are given in Appendix IV. These sites were selected because they were expected to give good nitrogen responses and did not have crusting problems. Therefore any structural improvement would not affect germination and introduce another variable into the trials.

The ammoniated sulfomethylated coal humates (ASHA) were tested in the field in comparison to other nitrogen sources. Because there was

no information to determine if the ammonium contained in the ASHA would nitrify, the ASHA was compared to both a nitrate source ($NaNO_3$) and an ammonium source $(NH_4)_2SO_4$. A blend of the ASHA was prepared with urea by the Alberta Research Council in the hope that this would form a high nitrogen content, slow release form of ASHA. This then required the inclusion in the test of a treatment containing urea. A check was included which had no applied nitrogen.

All fertilizer plots received a large amount of phosphorus, potassium, and sulphur to reduce the possibility of deficiencies of these elements restricting plant growth. The six treatments with four replicates applied at each of the four field sites were:

(1) check

(2) ammonium sulphate

(3) sodium nitrate

(4) urea

(5) ASHA

(6) ASHA blended with urea

All treatments received an application of P, K, and S. Rates of fertilizer applications are given in Appendix V. They were not the same at all sites because it was believed the sites with grass had a higher growth potential and were more likely to immobilize nutrients than the grain sites.

No information was available on the rate of release of bound forms of nitrogen in the coal humate molecule. The coal humate treatments were applied at Rich Valley on the basis of nitrogen which was expected to be available to the plant in its growth period (the available

distillable NH_4^+ and NO_3^- N plus urea N plus about 30% of the bound nitrogen within the coal molecule). The assumption that 30% of the bound nitrogen would become available was later felt to be high and reduced for the other sites. Analytical data on the forms and amount of nitrogen present in some of the ASHA products used are given in Appendix III.

Rich Valley and Dunstable sites were seeded to Galt barley on May 23 and 29, 1969 respectively. The land was rototilled prior to broadcasting fertilizer, then rototilled lightly again to about 5 cm deep and seeded with an experimental plot drill (Bentley, 1956). The phosphorus fertilizer was drilled in the row at the time of seeding. Plots 3.2 by 6.9 meters were arranged in a randomized complete block design. Each plot consisted of 18 rows 0.178 meters apart and 6.9 meters long. Roadways of about one meter in width were later made along the ends of the plots.

The Busby site had a stand of bromegrass (Bromus inermus) which was about six years old. The Fort Saskatchewan site was a well established lawn of Kentucky Blue Grass (Poa pratensis) and creeping red fescue (Festuca rubra). The grass at Busby was mowed, raked and fertilized on June 5, 1969. The lawn at Fort Saskatchewan was fertilized and watered on June 6, 1969. On June 8 the lawn at Fort Saskatchewan was mowed and all cuttings discarded, as they represented growth of the previous two weeks. At both the Busby and Fort Saskatchewan sites, the plots were square (3 meters to a side). These sites were also a randomized complete block design.

The grain plots had frost damage during the first week of June.

During the month of June it was quite dry, so both these sites were slow to recover after the frost damage. The bromegrass at Busby was slow to recover from the close mowing it received on June 6. Irrigation by sprinklers was undertaken on June 20 at Rich Valley, June 24 at Busby and June 26, 1969 at Dunstable. Approximately two inches of water was applied at each site. Rainfall was above normal for July, August, and September which resulted in good growth. The lawn site at Fort Saskatchewan was loamy sand, so it dried very quickly. It was watered by means of sprinklers during the summer. In July the town had severe water rationing so this site suffered from drought at that time.

During July the barley sites were hoed and hand weeded. The lawn at Fort Saskatchewan was sprayed at seeding with a selective herbicide (Mecoturf) to destroy dandelion (<u>Taraxacum</u> <u>officinale</u>) and traces of clover (<u>Trifolium</u> <u>repens</u>) that were present. The herbicide application was repeated twice during the summer. The grass at Busby suffered some rodent damage and poison was spread several times during the summer.

Plant samples were harvested during the growing season to determine if the nitrogen release varied over time between the different fertilizer sources. The samples were harvested with a sickle. The barley plots at Dunstable and Rich Valley were sampled in the milk stage, July 18 and 29, 1969 respectively, by means of harvesting two rows of barley, each 5.03 meters long. The second and final harvest was made at Rich Valley August 27 and at Dunstable on September 2 and 8, 1969. This consisted of taking four rows which did not border the edge of the plot or the previous area harvested.

The grass at Busby and lawn at Fort Saskatchewan were harvested by means of cutting a square of 1.22 meters by 1.22 meters. The grass at Busby was harvested twice, August 1 and September 16, 1969. The lawn at Fort Saskatchewan was harvested eight times with an electric hedge clipper.

Soil samples were taken to determine if the amounts of available nitrogen varied between treatments and to determine if any differences existed between the fertilizers with regard to leaching of nitrogen downward in the soil. Soil samples were taken at Rich Valley August 28 and November 4, 1969, at Dunstable July 29 and September 24, 1969, and at Fort Saskatchewan July 22, August 28, and November 4, 1969. The second soil sampling at Rich Valley was only 0 to 15 cm, as the previous results had shown very little additional nitrogen had moved below this depth because of a Solonetzic Bt horizon. The other samplings were taken to 60 or 75 centimeters deep.

The harvested plant materials were dried at 40° to 50° C. and their dry weights recorded. The second harvest of the grain plots was threshed and grain and straw weights were determined. Samples of plant materials were ground to 60 mesh size and subjected to Kjeldahl analysis according to Prince (1945), except that the catalyst was 9.9 grams K_2SO_4 , 0.41 grams HgO, and 0.08 grams $CuSO_4$. This method determined total nitrogen other than nitrate nitrogen. Soil samples were extracted with 2 N KCl solution and analyzed by steam distillation with MgO for determination of ammonium N and with MgO and Devarda alloy for determination of nitrite and nitrate N (Bremner, 1965).

The data for the randomized complete block field trials of

fertilizers were subjected to analysis of variance. Duncan's Multiple Range Test was used at the 5% level to statistically compare the means of different treatments.

The net recovery of fertilizer nitrogen by the crop was determined by deducting the nitrogen present in the crop on the check plot. Net recovery was then compared to the total available nitrogen applied as nitrate, ammonium, and urea. The plots which received coal humates received more total nitrogen than the other nitrogen treatments as the coal humate materials contained an additional 2 to 3% bound nitrogen which was not readily available. This bound nitrogen was not considered when calculations of application rates or uptake efficiencies were made.

Field Emergence Experiments

Damage to seedlings by heavy fertilizer applications is an important agricultural problem. Nitrogen applications in the row at 10 to 45 kg per hectare can reduce yields in dry years and delay emergence by one week (Nyborg and Hennig, 1969). If the soil is wet this damage to crops is not as pronounced. The coal humic acids contain nitrogen in a bound form and on exchange sites, so it was considered this might play a part in reducing the damage caused by nitrogen to the emergence of seeds. Work of Freeman and Fowkes (1969) showed that coal humates became toxic to plants when applied in excess of 0.8% in nutrient solutions. Because the possibility existed that the coal humate might reduce nitrogen damage to seedlings, but might be toxic itself, an emergence experiment was designed.

Two field sites were selected: at Rich Valley, a Grey Solonetz and at Dunstable, a Grey Gleysolic Luvisol. Locations and soil characteristics are given in Appendix IV. Galt barley (Hordeum vulgare) was planted at the rate of 110 kg per hectare and 3 cm deep. A single row push seeder designed for plot work was used. Seed and fertilizer were placed on the same V shaped belt and placed in the ground together. Each plot consisted of one row 6.9 meters long and a space of 0.3 meters was allowed between plots. Four replicates were made of each treatment and the experimental design was a complete randomized block.

Nitrogen was used as a fertilizer and the fertilizers were applied at rates to give 200 kg per hectare N. The ammoniated sulfomethylated coal humic acid (ASHA) had a low nitrogen content (Appendix III), so it was not feasible to use it as a nitrogen application because of the bulk of material which was needed to give this amount of nitrogen. The ASHA blended with urea (PHSC 8B) had a much higher nitrogen content so was feasible to apply at a rate to provide 200 kg per hectare N. The urea contained in the PHSC 8B introduced a problem of urea toxicity, so it was necessary to include a urea treatment. Another treatment consisted of ASHA (PHSC 6B) mixed with urea to approximate the composition of PHSC-8B. This was included to test if the preparation of the PHSC 8B differed from a physical mixture of ASHA and urea. Treatments were:

control - no fertilizer;

ammonium sulphate;

urea;

coal humate-urea blended (PHSC 8B);

coal humate (PHSC 6B) + urea, to give a similar amount of coal

humate and urea as was present in the PHSC 8B treatment.

The Dunstable site was seeded on May 29, Rich Valley on June 12. Both sites were quite dry at the time of seeding, but later received about two inches of water from sprinkler irrigation. The Rich Valley site was irrigated June 20 and the Dunstable site on June 26, 1969.

Emergence was recorded by counting barley plants present in a 2.4 meter section taken from each row. Counts were made June 27 at Dunstable and July 9 at Rich Valley. Counts of emergence were analyzed by a complete randomized block analysis of variance. Significant differences between means were identified by applying Duncan's Multiple Range Test at a 95% level of probability.

Greenhouse Experiments

Greenhouse experiments were set up to determine the ability of ammoniated sulfomethylated coal humic acids to supply nitrogen when low rates of nitrogen were applied. Khristeva (1963) suggested humic fertilizers functioned at the best efficiencies relative to chemical fertilizers when low rates of application were used. An experiment was set up to determine the ability of the ASHA to supply sulphur to plants grown on sulphur-deficient soils. Other greenhouse experiments were set up to determine if the coal humates had any ability to improve acid soils with respect to reducing plant damage caused by aluminum toxicity. Russell (1966) reported organic matter had considerable ability to chelate aluminum. Hoyt (1970) found that alfalfa or sugar additions to soil reduced impediments to plant growth caused by aluminum toxicity.

<u>Nitrogen and Sulphur Supplying Power of Ammoniated Sulfomethylated Coal Humic Acids</u>

An experiment designed to test both the nitrogen and sulphur supplying power of ASHA was conducted in the greenhouse on Braeburn soil. Braeburn is a loam to clay loam Grey Luvisol. It was shown to give large plant growth responses to both nitrogen and sulphur fertilization (Nyborg, 1968). The sample chosen was an A_p horizon from an area that had been cultivated about 15 years. This soil had a pH of 6.

The treatments applied were:

(1) PKS

(2) N(15 ppm)PKS

(3) N(30 ppm)PKS

(4) ASHA(15 ppm N)PKS

(5) ASHA(30 ppm N)PKS

(6) NPKS

(7) NPK (S as coal)

(8) NPK

Details of chemicals applied are given in Appendix VI.

The first five treatments were designed to test if the ASHA conferred any benefits on nutrient efficiencies when at low rates of application. On these treatments P, K, and S were supplied to prevent interference from other nutrient deficiencies. Nitrogen was applied at 15 and 30 ppm as ammonium chloride or as ASHA. These rates of nitrogen application were minimal, so plant growth would soon be under stress for lack of nitrogen.

The treatments numbered 6, 7, and 8 were designed to test if the coal humates had any sulphur supplying potential. The ASHA con-

tained 2% sulphur. The ASHA was applied at a rate to supply 25 ppm S. Nitrogen was applied at 80 ppm with the anticipation this would provide more nitrogen than was needed for plant growth. However, the ASHA (treatment 7) contained about 30 ppm N in excess of treatments 6 and 8.

Plastic pots, each containing 1500 grams of air dry soil were used. The nitrogen and sulphur fertilizers were applied as an aliquot of solution except for the coal humates which were applied as a 60 mesh powder. PK solutions were banded 1.5 inches deep. Husky barley (*Hordeum vulgare*) was planted 3/4 inch deep. Ottawa sand was used to cover holes where the barley seeds were placed in order to prevent soil crusting. The plants were grown 49 days with water added to keep the soil at 70% to 100% of field capacity.

The treatments 1 to 8 were made up with three replicates and grouped in a randomized complete block design. Oven dry weights of the harvested plant material were recorded. The total nitrogen content of the dry material was determined according to the Kjeldahl procedure (Prince, 1945) with the modifications outlined under Field Fertilizer Experiment Methods (page 22).

Total sulphur in the plant material was determined by the wet digestion method of Johnson and Ulrich (1959) and measurement of sulphur in the digests was by the micro distillation method of Dean (1966).

Total plant dry matter yields, nitrogen yields, sulphur yields, and N/S ratio were determined. A randomized complete block analysis of variance was applied to the various categories of data. Treatment differences were compared by means of Duncan's Multiple Range Test applied at the 95% level of probability.

Ability of Coal Humic Acids to Alleviate Soil Acidity Damage to Crops

Russell (1966) reported that additions of humus materials had considerable ability to reduce soluble aluminum. Hoyt (1970) found that organic additives, chopped alfalfa and sugar, reduced soil acidity damage on a high aluminum acid soil. It was reported from the USSR (Khristeva, 1963) that coal humates and other organic manures were responsible for increased plant growth on a number of types of soils including Podzols and Sod Podzols. These two types of soils are usually quite acid. From this it was assumed coal humates might play a role in alleviating retardation of plant growth on acid soils where soluble aluminum was the major plant growth impediment.

Those aluminum ions that are found in the soil solution or are easily displaced from the soil exchange system or from amorphous gels are referred to as soluble aluminum. Soluble aluminum is both a cause and a consequence of low soil pH. It plays a major role in restrictions of plant growth that may occur on acid soils. One of the causes of this growth restriction appears to be aluminum ions hindering the translocation of calcium from plant roots to the rest of the plant.

Two greenhouse pot experiments were conducted on acid soils. The first used barley to compare the ability of coal humates and lime in alleviating crop damage due to soil acidity. In the second experiment alfalfa was grown on three different soils. These soils were chosen because they were all acid and they covered a wide range of soluble aluminum values.

Pot Experiment with Barley Grown on an Acid Soil

A Humic Eluviated Gleysol of the Josephine series (Reeder and Odynsky, 1965) was used for this experiment. The organic horizons had been destroyed by clearing and the A_p horizon was used. This soil was high in soluble aluminum (29.6 ppm). Husky barley was used as a crop because it is sensitive to soluble aluminum above 2 to 4 ppm, but not sensitive to manganese toxicity (Hoyt and Nyborg, 1970).

Previous work on this soil (Nyborg, 1970) showed that barley yields were three times as large when the plants were supplied with a nitrate N source as compared to an ammonium nitrogen source. Because of this yield depression by an ammonium nitrogen source it was not desirable to use an ammonium humate to alleviate soil acidity damage. This soil was shown to give good responses to lime applications. Therefore it was believed a calcium humate would best serve to reduce soil acidity damage.

A calcium salt of sulfomethylated coal humate was prepared from the ammonium salt of PHSC 10B (Appendices I and III) by adding 136 grams calcium hydroxide to 908 grams of the NH_4^+ salt of PHSC 10B. A solution of this was prepared with 5 liters of water and evaporated to dryness at a temperature of 60° C. This process evaporated off most of the NH_4^+ in the coal humate. The calcium humate had a pH of 8.9 as compared to 5.9 for the ammonium humate, and the calcium humate was only slightly water soluble as compared to 90% solubility of the ammonium humate.

The calcium salt of humate was used as a soil amendment. It was compared to calcium applied as calcium hydroxide to provide the

same pH as the calcium humate. Another treatment was an equal amount of humate, applied in the ammonium form. One treatment was limed to neutrality and an unaltered control was included. All treatments received a nitrogen application of 120 ppm N from $Ca(NO_3)_2$ which was applied in solution and mixed with the soil. KH_2PO_4 was applied to give 40 ppm P and 50 ppm K. This was banded in the pots at 1 1/2 inches below the final soil surface. Treatment details are given in Appendix VII. Four replications were made of each treatment and the experimental design was a complete randomized block.

Husky barley (Hordeum vulgare) was seeded February 16, 1970 and grown until April 13. The plants were provided with 18 hours of light daily and temperatures were kept between 13° and 25° C. The plants were watered to keep moisture levels between 60% and 100% of field capacity (28.8% water).

Plants were harvested by clipping them 2 cm above the soil surface. Plant materials were dried at 70° C. and oven dry weights were recorded. The dry weights of the harvested plant materials were analyzed by a complete randomized block analysis of variance. Duncan's Multiple Range Test was used at a 95% level of probability to distinguish significant differences between treatment means.

The soil pH was determined on fresh samples taken at harvest. The method of pH determination used consisted of taking one part soil and 2.5 parts water. This was stirred for half an hour and allowed to settle for one hour. The hydrogen electrode was placed in the sediment and the reference electrode in the supernatant solution. Soluble aluminum and manganese were measured by the Alberta Soil and Feed Test-

ing Lab. The method consisted of extracting soil for one hour in a mixture of two parts 0.02 M $CaCl_2$ and one part soil and determining soluble aluminum and manganese on the extract.

Pot Experiment with Alfalfa Grown on Acid Soils

This experiment was designed to test if the effect coal humates had on the growth of plants on acid soils was related to the presence of soluble aluminum in the soil. Because of the sensitivity of young alfalfa plants to aluminum toxicity (Dawson, 1958), Ladak alfalfa (*Medicago sativa*) was used as an indicator of aluminum toxicity on the three acid soils. The soils were chosen because they varied in amounts of exchangeable aluminum. The soils were:

(1) a Humic Eluviated Gleysol, Josephine series (Reeder and Odynsky, 1965) which had organic horizons destroyed, the texture was loam, the pH was 4.8 and this soil was high in soluble aluminum.

(2) a Grey Solod, Alcan series (Farstad, Lord, Green, Hortie, 1965), the texture was silt loam, the pH was 5.1 and this soil was intermediate in soluble aluminum.

(3) a Grey Solod, Alcan series, the texture was silty clay loam, the pH was 5.5 and this soil was low in soluble aluminum.

Growth of alfalfa after an application to the soil of calcium salt of coal humate (PHSC 10B) was compared to growth of alfalfa when $Ca(OH)_2$ was applied. The calcium humate was prepared according to the method outlined under Pot Experiment with Barley Grown on Acid Soils. The $Ca(OH)_2$ applications were made at rates estimated to bring the

soils to the same pH as the soils which were treated with calcium humate. The treatments consisted of:

Josephine loam + 0.70% calcium humate

Josephine loam + 0.096% calcium hydroxide

Alcan silt loam + 0.35% calcium humate

Alcan silt loam + 0.048% calcium hydroxide

Alcan silty clay loam + 0.35% calcium humate

Alcan silty clay loam + 0.048% calcium hydroxide

The calcium humate and $Ca(OH)_2$ were added as a powder and mixed with the dry soil. Sealed plastic greenhouse pots were used, each containing 1500 grams of air dry soil. A fertilizer solution was mixed with the soil. This solution supplied 60 ppm N, 168 ppm K, 10 ppm S, 1 ppm B, and 0.01 ppm Mo. A solution of KH_2PO_4 application was banded one inch deep to supply 40 ppm of P and 50 ppm of K. On March 23 Ladak alfalfa was planted in holes 1/2 inch deep and covered with Ottawa sand. The soil was watered to keep the moisture content between 70% to 100% of field capacity. The plants received 12 to 15 hours of light daily, temperatures were quite variable and ranged from 12° to 30° C. The alfalfa was harvested June 8 by cutting 2 cm above the ground. Plants were dried at 70° C. and oven dry weights were recorded. The dry weights of the plant material were analyzed by a complete randomized block analysis of variance. Duncan's Multiple Range Test was used at the 95% level of probability to distinguish significant differences between treatment means.

It was desired to determine if alteration of plant growth by an amendment was due to shift in pH or to a change in amounts of soluble aluminum in the soil. For these reasons, after harvest of the

plant material, the soils were analyzed to determine the amount of soluble aluminum and the pH. The Alberta Soil and Feed Testing Lab did tests on duplicate soil samples for $CaCl_2$ soluble aluminum and manganese. The soil pH was determined on fresh samples taken immediately after harvest. The methods of pH and $CaCl_2$ soluble aluminum and manganese determination were the same as outlined under Pot Experiments with Barley Grown on Acid Soils, Materials and Methods.

Structural Effects of Organic Amendments to Soil

Sulfomethylated coal humic acids have some unusual properties which led to speculation that they might serve as amendments to improve structure in some soils. Sulfomethylated coal humic acids were known to have considerable ability to disperse bentonite drilling muds and had been used as a mud thickening agent in the oil drilling industry. The coal humates were believed to have a structure somewhat similar to soil humic acids, which play a major role in formation of good soil structure. The ammonium salt of sulfomethylated coal humic acid was water soluble, but exhibited low wettability. The foregoing characteristics made it uncertain how coal humic acids might affect soil structure and made it necessary that soil structural experiments be included as part of an agricultural evaluation of coal humates. Little information was available in the literature on the effects of coal humates on soil structure, and no information was available concerning the effect of the water soluble ammoniated sulfomethylated coal humates.

If coal humates could cause structural improvements and act as a slow release fertilizer, they could be an especially valuable fertilizer for use on poor structured soils. Alberta has large areas of agricultural

land classified as Solonetzic and Luvisolic soils, which have important structure problems.

Aggregate Analysis Experiments

Water stable aggregation of the experimental soils was determined because one of the structural problems of Solonetzic and Luvisolic soils is that they slake on wetting and then dry to form either a massive or a structureless soil. Such characteristics may result in soil crusting or may result in a soil which erodes easily. Increased aggregation should improve soil drainage and provide a better environment for root development.

Sulfomethylated coal humic acids (PHSC 10B) (Appendices I, II, and III) were added to three soils. The soils were:

- a Bt horizon from a Duagh Black Solonetz (Bowser, Kjearsgaard, Peters, and Wells, 1962), a silty clay loam in texture, which formed very hard massive lumps on drying, and was almost impermeable to water;
- an Ap horizon from a Nampa Grey Solod (Reeder and Odynsky, 1965), a clay loam in texture, which formed a massive structure and crusted badly; and
- an Ap horizon from a Black Solod from near Stettler, Alberta, a loam in texture which tended to crust, and on drying was rather structureless.

These soils represented decreasing degrees of structural impairment.

For comparison with the structural effect of coal humic acids, Orzan lignin products were included in the experiment. Two Orzan products were used: Orzan A, an ammonium salt of lignin; and Orzan S, a sodium

salt of lignin. The Orzan products were produced by Crown Zellerbach Co. Ltd., Camas, Washington, from lignin wastes derived from the bisulphite paper manufacturing process.

The treatments added (by weight) to the soils were:

control

coal humate PHSC 10B - 2.0%

coal humate PHSC 10B - 0.2%

Orzan A - 2.0%

Orzan A - 0.2%

Orzan S - 2.0%

Orzan S - 0.2%

Orzan S was only used on the Nampa soil.

The soils were air dried and ground to pass a 2 mm size screen. The additives were mixed with 500 grams of air dry soil and placed in an aluminum food dish 15 cm in diameter and 4 cm deep. Eight replicates were prepared of each soil and treatment. The soils were kept at temperatures ranging from 10° to 20°C. and were watered by weight to field capacity about every week. The mixtures of soils and additives were prepared October 10 and aggregate analysis was conducted about five weeks later.

Soil samples were also taken at the site of the Rich Valley field fertilizer experiment (Appendix IV) from the coal humate (PHSC 10B) and $(NH_4)_2SO_4$ fertilized plots. These samples were analyzed for water stable aggregates in a similar manner to the samples taken from aluminum dishes. The barley plots were fertilized May 23, 1969 (Appendix V). Soil samples were taken from the 0 to 15 cm depth November 4, 1969 about

ten weeks after harvest of the barley. It was hoped to determine if a low rate of application of ASHA had any effect on soil structure after six months of incubation in the soil.

Aggregates were measured by a wet sieving procedure (Kemper and Chepil, 1965). Moist soil was passed through a 1.25 cm screen to obtain large aggregates. The aggregates were air dried and approximately a 20 gram sample placed upon a nest of six sieves with sizes of 5, 9, 16, 32, 60, and 115 mesh. The sieves were rapidly immersed in distilled water at room temperature. The samples were allowed to soak for ten minutes and were then shaken for ten minutes. The oven dry weights of the aggregates remaining on the screens were used to compute the mean weight diameter of aggregates according to the graphical procedure outlined by Van Bavel (1950).

Soil Crusting Experiments

Soil crusting was a severe problem on the Nampa and Duagh soils and a slight problem on the Black Solod. Crusting occurs on soils which slake easily. Crusting may greatly reduce seedling emergence of cereal and forage crops.

To make measurements of crust strength, a pocket penetrometer was used (Davidson, 1965). This penetrometer consisted of a springloaded steel shaft 0.64 cm in diameter. A pressure reading was made of soil crust strength prior to rupture by the shaft.

The same soils prepared for aggregate analysis were used for crusting measurements (Aggregate Analysis Experiments, Materials and Methods). Three penetrometer readings were taken on each aluminum dish of soil that had been prepared for aggregate analysis. Eight replicates

of soil were used for each treatment.

The pocket penetrometer method provides an approximate determination of crust strength. When the soil dried, the coal humates tended to migrate to the surface forming a layer of coal humate which sometimes became detached from the soil surface. This detached surface crust had an extremely variable strength as measured by the pocket penetrometer.

To give an indication of soil crust strength, Modulus of Rupture, according to the procedure of Reeve (1965), was tried. The briquets prepared from soil treated with coal humates were not flat when dried. Because curved briquets from coal humate treated soil could not be compared on the basis of Modulus of Rupture to the flat briquets formed from the other treatments, experimental work on Modulus of Rupture was discontinued.

Hydraulic Conductivity Experiment

The literature does not contain reports on how sulfomethylated coal humates affect hydraulic conductivity of soils. If coal humates function in a manner similar to humus materials, or to synthetic linear organic polymer aggregating agents such as Krilium or Vama, they should improve hydraulic conductivity. If sulfomethylated coal humates act as a dispersing agent, as they do with bentonite drilling muds, or if the low wettability characteristics predominate when they are mixed with soils, then the coal humates will reduce soil drainage and hydraulic conductivity. Many of the soils which might receive structural benefits from additions of coal humate have low hydraulic conductivity. For coal humates to be used as an additive on such soils, they must not impair internal drainage and should improve it.

To measure the internal drainage characteristics of soils treated with coal humates, hydraulic conductivity was determined according to the method of the USA Salinity Laboratory Staff (1954). Two soils were used: a clay loam Ap horizon from the Nampa series; and a loam, Ap horizon from a Black Solod. They are two of the same soils described in the discussion on Aggregate Analysis Experiments, Materials and Methods. The soils were air dried and ground to 2 mm size.

Sulfomethylated coal humic acids in the ammonium and calcium forms were used as treatments in the hydraulic conductivity experiment. A calcium salt of ASHA was prepared (Greenhouse Experiments, Materials and Methods). The ammonium salt of rusty coal (PHSC 6A) was also used as a treatment (Appendix I). To provide a comparison of the effect of the cations present in the NH_4 and Ca humates, NH_4Cl and $CaCl_2$ were included in the test. NH_4Cl and $CaCl_2$ were applied at rates which provided equal amounts of NH_4 and Ca as the NH_4 humate and Ca humate, respectively. As another organic additive, lignin compounds formed from the bisulphite paper manufacturing process were used. Two compounds -- Lignisol TSD, an ammonium salt of lignin, and Lignisol BD, a calcium salt of lignin -- were included in the experiment. The Lignisol compounds were supplied by Lignisol Chemicals, Quebec, Quebec.

The treatments used on the Nampa and the Black Solod soils (by weight) were: control

NH_4Cl - 0.11%

$CaCl_2$ - 0.22%

NH_4 coal humate (PHSC 10B) - 1.0%

Ca coal humate - 1.0%

NH_4 rusty coal - 1.0%

NH_4 lignin (Lignisol TSD) - 1.0%

Ca lignin (Lignisol BD) - 1.0%

To determine hydraulic conductivity, 150 grams of treated soil were added to a 5.0 cm diameter plastic cylinder. The soils were saturated with deionized water by soaking the base of the cylinders in water for 24 hours. After saturating the soil, a constant head of 22 cm of dionized water was maintained. Flow rate was measured for 48 hours and hydraulic conductivity was determined from the flow rate after 48 hours. That length of time was used because flow rates did not stabilize until about two days had elapsed.

RESULTS AND DISCUSSION

Fertilizer Experiments

Field Plot Experiments

Four experiments were conducted, two on barley, one on bromegrass, and one on a lawn. Coal humates were compared to other nitrogen sources to determine if any slow release of nitrogen occurred and if any stimulation of growth by the coal humates occurred. All the crops grown on field experiments showed good growth responses to additions of nitrogen fertilizers.

Rich Valley Barley Plots

Plant dry matter yields and plant nitrogen yields are presented in Table 1, available soil nitrogen yields in Table 2, and net recoveries of nitrogen in Table 3. The plots fertilized with coal humates (PHSC 6F) did not significantly differ from the other nitrogen fertilized plots in their harvest dry matter yields and the yield of total nitrogen present in the grain. However, the nitrogen present in the straw on the PHSC 6F plots was significantly less than the straw from the other nitrogen fertilized plots. This can be explained because the PHSC 6F plots received less available nitrogen than the other nitrogen fertilized plots. The plots fertilized with coal humate blended with urea (PHSC 8A) gave yields of plant material and plant nitrogen which did not differ significantly from urea or the other chemical nitrogen sources. In the final harvest, net nitrogen recoveries by the plants grown on the fertilized plots was about 50% to 60% of the applied nitrogen. Net recovery of nitrogen by the plants was determined by taking the total nitrogen present in the plant material from the fer-

Table 1. Yield and Uptake of Nitrogen for Barley at Two Stages of Growth, Rich Valley Site.

		Barley harvested at milk stage (July 18)		Barley harvested at maturity (August 27)			
Treatment	Available N applied kg/ha	Yield of dry matter 100 kg/ha	Uptake of N kg/ha	Yield of grain 100 kg/ha	Yield of grain + straw 100 kg/ha	Uptake of N in straw kg/ha	Uptake of N in grain kg/ha
Check	0.0	* 8.0b	15.1c	12.7b	25.2b	5.2c	21.1b
$(NH_4)_2SO_4$	100.9	11.9a	32.1b	26.3a	53.1a	22.2a	60.9a
$NaNO_3$	100.9	12.8a	38.8ab	25.3a	50.7a	22.6a	55.9a
Urea	100.9	12.9a	39.5a	24.6a	48.0a	21.3ab	57.9a
Coal humate (PHSC 6F)	74.5	12.8a	35.5a	24.7a	49.6a	17.5b	51.9a
Coal humate + urea(PHSC 8A)	86.7	14.0a	39.6a	24.4a	49.8a	21.5ab	54.5a
		$**S\bar{x}=0.94$	$S\bar{x}=1.90$	$S\bar{x}=1.69$	$S\bar{x}=3.51$	$S\bar{x}=1.36$	$S\bar{x}=1.69$

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.

** Standard error of the mean.

Table 2. Soil Nitrogen (Ammonium + Nitrate) in the Top 15 cm of Soil on Different Treatments, Sampled November 4, Ten Weeks After Harvest, Rich Valley Site.

Treatment	NH_4 N kg/ha	NO_3 N kg/ha	Total
Check	* 4.5b	2.2	6.7
$(NH_4)_2SO_4$	9.3a	5.5	14.7
$NaNO_3$	5.4b	8.6	14.0
Urea	10.0a	6.3	16.3
Coal humate (PHSC 6F)	5.9b	3.2	9.1
Coal humate + urea (PHSC 8A)	5.2b	5.5	10.7
	$**S\bar{x}=0.87$	$S\bar{x}=2.15$	$S\bar{x}=2.35$

Note: Values reported only for the 0 to 15 cm depth, because due to a Solonetzic Bt horizon, no appreciable NH_4 or NO_3 N was found below that level.

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.

** Standard error of the mean.

---

tilized plots less the total nitrogen in the plant material from the check plots.

In November the plots fertilized with coal humate (PHSC 6F) had a net increase of available soil nitrogen of 2.4 kg per hectare which compared with a net increase of 7.3 to 9.6 kg per hectare for the three chemically fertilized plots. The lower recovery of available nitrogen in the soil on the plots fertilized with PHSC 6F can be explained by the lower amounts of available nitrogen which was applied to these plots. The low amount of available soil nitrogen on the plots fertilized with PHSC 6F also indicates little release of the bound forms of nitrogen present in the coal humates.

Table 3. Net Recovery of Applied Nitrogen in Barley at Two Stages of Growth and in the Soil Eight Weeks After Harvest, Rich Valley Site.

		* Net Recovery of Applied Nitrogen				
Treatment	Available N applied kg/ha	In barley at milk stage kg/ha	In mature barley kg/ha	**In the soil Nov. 4 kg/ha	Net recovery in mature barley as a % of applied available N	Total net recovery in mature barley + soil, as % of applied available N
Check	0.0	0.0	0.0	0.0	0.0	0.0
$(NH_4)_2SO_4$	100.9	17.0	56.7	8.0	56.2	64.1
$NaNO_3$	100.9	23.8	52.2	7.3	51.7	59.0
Urea	100.9	24.4	52.8	9.6	52.3	60.9
Coal humate (PHSC 6F)	74.5	20.5	43.0	2.4	57.7	60.9
Coal humate + urea (PHSC 8A)	86.7	24.6	49.6	4.0	57.2	61.8

* Calculated as nitrogen in fertilized treatment minus nitrogen in check.
** As NH_4 nitrogen plus NO_3 nitrogen.

Dunstable Barley Plots

On the Dunstable plots the barley growth was good and heavy yields of grain and straw resulted in almost total net uptake of the applied fertilizer nitrogen (Tables 4 and 6). In both the July and September, 1969 harvests more nitrogen was taken up by the barley on the plots fertilized with $NaNO_3$ than on the other nitrogen fertilizer plots. This was, apparently, luxury consumption as it did not cause increased yields in the September harvest. The coal humate plots (PHSC 6B) yielded less and showed less uptake of nitrogen than the chemically fertilized plots. The coal humate plots received 96.6 kg per hectare of available nitrogen as compared to 100.9 kg per hectare available nitrogen on the chemically fertilized N plots. This difference in supply of available N was not large enough to explain the lesser plant yield and uptake of nitrogen in the coal humate plots and this difference in uptake indicated available nitrogen applied in the coal humate was not completely available to plants in the growing season at this site. Crop recoveries of nitrogen for the chemically fertilized plots was about 100% or greater, which was exceptionally high and contrasted with Allison's (1966) statement that these seldom exceeded 70%. This high recovery could be accounted for by the following conditions:

- nitrogen fertilizers stimulating plant growth resulted in a plant obtaining nutrients from a larger area than the check;
- increased soil nitrogen from fertilizers resulted in greater microbial action and greater release of soil organic nitrogen;
- a heavy textured subsoil prevented any leaching losses;
- the soil pH was about 6. At this pH gaseous losses were a minimum.

Table 4. Yield and Uptake of Nitrogen for Barley at Two Stages of Growth, Dunstable Site.

		Barley harvested at milk stage (July 29)		Barley harvested at maturity (Sept. 2 and 6)			
Treatment	Available N applied kg/ha	Yield of dry matter 100 kg/ha	Uptake of N kg/ha	Yield of grain 100 kg/ha	Yield of grain + straw 100 kg/ha	Uptake of N in straw kg/ha	Uptake of N in grain kg/ha
Check	0.0	*10.6b	14.8c	17.8c	32.4c	8.9d	41.5c
$(NH_4)_2SO_4$	100.9	24.8a	59.7b	44.0ab	85.4a	38.5ab	113.5a
$NaNO_3$	100.9	27.2a	81.7a	45.2a	90.9a	45.5a	117.8a
Urea	100.9	25.2a	67.2b	47.0a	89.2a	32.8bc	117.4a
Coal humate (PHSC 6B)	96.6	23.8a	60.4b	38.9b	74.1b	23.9c	92.9b
Coal humate + urea(PHSC 8B)	97.3	24.3a	58.3b	43.0ab	83.8b	33.7b	108.7ab
		**$S\bar{x}$=1.85	$S\bar{x}$=4.17	$S\bar{x}$=1.69	$S\bar{x}$=13.29	$S\bar{x}$=2.88	$S\bar{x}$=5.86

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.

** Standard error of the mean.

Table 5. Soil Nitrogen (Ammonium + Nitrate) in the Different Fertilizer Treatments, Sampled September 24, Three Weeks After Harvest, Dunstable Site.

Treatment	0-15 cm (NH_4 + NO_3) N kg/ha	15-60 cm (NH_4 + NO_3) N kg/ha	Total (NH_4 + NO_3) N kg/ha
Check	6.0	4.4	10.4
$(NH_4)_2SO_4$	7.6	2.8	10.3
$NaNO_3$	6.5	2.7	9.2
Urea	6.2	3.9	10.1
Coal humate (PHSC 6F)	7.1	5.0	12.1
Coal humate + urea (PHSC 8A)	6.3	4.5	10.8

When the six treatments were compared on September 24, 1969 the difference in available soil nitrogen was not great (Table 5). Slightly more net soil nitrogen was present in the PHSC 6B plots indicating a very slight slow release of nitrogen. A test of soil nitrogen from samples collected the following April 30 showed no change in available nitrogen indicating no further release of nitrogen.

Busby Bromegrass Plots

Nitrogen fertilized bromegrass plots at Busby yielded from 2210 to 3080 kg per hectare of dry matter, as compared to 1480 kg per hectare for the control plots (Table 7). The coal humate (PHSC 6B) plots yielded 2380 kilograms per hectare, which did not differ significantly from the $(NH_4)_2SO_4$ plots and the urea plots. At both harvests the bromegrass showed significantly increased growth in response to sodium

Table 6. Net Recovery of Applied Nitrogen in Barley at Two Stages of Growth and in the Soil Three Weeks After Harvest, Dunstable Site.

		* Net recovery of applied nitrogen				
Treatment	Available N applied kg/ha	In barley at milk stage kg/ha	In mature crop kg/ha	**In the soil Sept. 24 kg/ha	Net recovery in mature barley as a % of applied available N	Total net recovery in mature barley + soil as % of applied available N
Check	0.0	0.0	0.0	0.0	0.0	0.0
$(NH_4)_2SO_4$	100.9	44.9	99.6	0.0	98.7	98.7
$NaNO_3$	100.9	66.9	112.9	-1.3	111.9	110.6
Urea	100.9	52.3	99.6	-0.3	98.7	98.4
Coal humate (PHSC 6B)	96.6	45.5	66.1	1.7	68.4	70.2
Coal humate + urea(PHSC 8B)	97.3	43.5	91.8	0.2	94.3	94.6

* Calculated as nitrogen in fertilizer treatment minus nitrogen in check.
** As NH_4 nitrogen plus NO_3 nitrogen.

Table 7. Yields from Bromegrass Plots, Busby Site

Treatment	Available N applied kg/ha	First harvest yield 100 kg/ha	Second harvest yield 100 kg/ha	Total yield 100 kg/ha	Nitrogen yield second harvest kg/ha
Check	0.0	*10.7c	4.1c	14.8c	10.6c
$(NH_4)_2SO_4$	145.7	15.0b	7.0b	22.1b	20.2b
$NaNO_3$	145.7	21.8a	9.0a	30.8a	26.4a
Urea	145.7	16.2b	7.7a	24.0b	22.4ab
PHSC 6B	139.6	16.5b	7.3ab	23.8b	21.1ab
PHSC 8B	130.9	18.4ab	7.7a	26.1ab	21.6ab
		**$S\bar{x}$=1.45	$S\bar{x}$=0.51	$S\bar{x}$=1.76	$S\bar{x}$=1.59

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.

** Standard error of the mean.

nitrate as compared to the other nitrogen fertilizers. The analysis of the plant material from the second harvest showed small differences in nitrogen uptake among the various fertilizer treatments. Net recoveries of nitrogen for this site were not high due to the rather limited growth of grass. This poor growth was due to it being an old stand of brome-grass and also to drought in the month of June.

At this site the coal humate (PHSC 6B) and the urea-coal humate (PHSC 8B) did not give plant growth responses different from ammonium sulphate and urea.

Fort Saskatchewan Lawn Plots

At Fort Saskatchewan grass yields were low on all plots, but when total yields for the summer were considered, the fertilized plots showed five times the grass yield of the check plots (Table 8) and 8 to 12 times the nitrogen yield when compared to the check plots (Table 10). Plots fertilized with sodium nitrate produced significantly larger yields than the plots which received other nitrogen fertilizers. Plant samples from the first two harvests were accidentally destroyed, so it was not possible to obtain nitrogen yields for these harvests. In addition, the samples from the check plots of the fourth harvest were too small for nitrogen analysis, and therefore nitrogen content was estimated. Total nitrogen recovered by the grass for the last six harvests was not high (Table 10). If one were to estimate total nitrogen for the first two harvests (based on average nitrogen content of the other harvests), and combine this with data from the last six harvests, total net nitrogen

Table 8. Yields of Lawn Grass, Fort Saskatchewan Site.

	Grass yields, 100 kg/ha								
Treatment	June 24	July 8	July 16	July 28	Aug. 8	Aug. 15	Sept. 2	Sept. 20	Total
Check	1.6	*0.4b	0.3c	0.2c	0.5b	0.2b	0.5c	0.8	4.4c
$(NH_4)_2SO_4$	4.6	2.8ab	1.1abc	2.3b	4.6a	1.9a	1.6b	1.6	20.5b
$NaNO_3$	3.1	4.2a	1.7a	3.8a	5.6a	2.0a	3.1a	2.1	26.5a
Urea	3.9	2.8ab	1.2ab	2.6b	4.3a	1.7a	2.5ab	2.0	20.9b
Coal humate (PHSC 6B)	3.6	2.1ab	0.9abc	2.8ab	5.2a	2.5a	2.4ab	1.6	21.3b
Coal humate + urea(PHSC 8B)	3.3	3.4a	0.8bc	2.8ab	4.7a	2.2a	1.6b	2.2	21.0b
	**$S\bar{x}$=0.69	$S\bar{x}$=0.72	$S\bar{x}$=0.27	$S\bar{x}$=0.34	$S\bar{x}$=0.57	$S\bar{x}$=0.34	$S\bar{x}$=0.33	$S\bar{x}$=0.40	$S\bar{x}$=1.02

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.

** Standard error of the mean.

Table 9. Ammonium + Nitrate Nitrogen in the Soil at Fort Saskatchewan at Different Sampling Dates.

Treatment	July 22		August 28		November 4	
	0-15 cm kg/ha	15-60 cm kg/ha	0-15 cm kg/ha	15-60 cm kg/ha	0-15 cm kg/ha	15-90 cm kg/ha
Check	9.4	13.4	2.4	10.3	6.0	14.3
$(NH_4)_2SO_4$	20.8	41.6	5.0	21.8	7.4	28.2
$NaNO_3$	22.0	30.2	4.2	10.5	6.8	15.7
Urea	17.3	16.8	4.9	16.9	7.1	19.4
Coal humate (PHSC 6B)	16.5	20.0	5.2	12.0	7.5	19.6
Coal humate + urea (PHSC 8B)	20.8	22.3	4.6	10.3	7.7	16.8

Table 10. Net Recovery of Applied Nitrogen in Lawn Grass and in the Soil Six Weeks After Final Lawn Harvest at Fort Saskatchewan Site.

Treatment	Available N applied kg/ha	***N in grass for six harvests kg/ha	Net N recovery in grass kg/ha	Net N recovery in soil Nov. 4 kg/ha	Net N recovery in soil and grass (6 cuts) as a % of applied available N
Check	0.0	* 6.1c	0.0	0.0	0.0
$(NH_4)_2SO_4$	168.0	49.9b	43.8	15.2	35.1
$NaNO_3$	168.0	74.9a	68.8	2.2	41.8
Urea	168.0	54.4b	48.3	6.2	32.4
Coal humate (PHSC 6B)	161.0	63.0ab	56.9	6.8	39.6
Coal humate + urea (PHSC 8B)	151.0	55.3b	49.2	4.2	35.4
		**$S\bar{x}$=5.55			

* In column values not followed by the same letter are significantly different at the 95% level of probability.

** Standard error of the mean.

*** Nitrogen data not obtained for the first two harvests.

recoveries for all eight harvests would range from 41% for the $(NH_4)_2SO_4$ plots to 47% for the coal humate (PHSC 6B) plots, and to a high of 56% for the plots fertilized with $NaNO_3$.

Grass grown on ammonium sulphate plots showed low recoveries of nitrogen, particularly late in the growing season (Table 9). Nevertheless, in August and November more available soil nitrogen was found in the plots fertilized with ammonium sulphate than in the plots fertilized with the other nitrogen sources. I would suspect this nitrogen was held in the soil in some manner not as readily available to the grass as the nitrate nitrogen.

Efficiencies of total soil and crop recovery of nitrogen were slightly lower for the urea and PHSC 8B plots. When urea was applied on this site gaseous losses of ammonia could be expected as the soil pH was high (pH 8.0). The PHSC 6B ammoniated coal humate showed good plant yields over time and evidence of a slight slow release of nitrogen.

Summary

The data from the field fertilizer experiments showed that ammoniated coal humates and a urea blend of this material, when considered on the available nitrogen basis, were about equivalent to standard chemical nitrogen forms with respect to nutrient release and plant growth. Any slow release properties the coal humates had were too small to be important when considered over one growing season.

When the coal humate fertilizers were applied to barley and

grass, no evidence was found that they had any special growth stimulatory properties other than that due to the nitrogen they contained. These findings agreed with those of Hoyt (1968) and Kozhekov, Lazareva, Abasova, Kulikova, and Kovaleva (1968) who concluded the plant growth response for organic additions was similar to the growth response obtained from the chemical nutrients contained within the organic additions.

When nitrate was used as a fertilizer, the lawn and bromegrass sites showed increased plant growth over plots fertilized with other nitrogen fertilizers. This increased growth was in response to increased uptake of nitrogen by the plants. The barley straw at the Dunstable site on the plots treated with sodium nitrate showed evidence of luxury consumption of nitrogen. This resulted in increased nitrogen content of the straw but no increase in yield. At these three sites reasons were not established for the increased efficiency of plant uptake of nitrate over other nitrogen fertilizers. The literature is quite inconclusive about efficiencies of uptake by plants of different forms of nitrogen in fertilizers (Allison, 1966).

Field Emergence Experiment

This experiment was designed to test if the coal humate reduced damage to seedlings caused by placement of nitrogen fertilizers with the seed. Also it was desired to know if the coal humate itself had an unfavorable effect on the seed or seedling when placed with the seed. Two field sites were planted to Galt barley and barley seedling emergences were recorded about four weeks after planting.

The results showed that emergence of barley seedlings was

Table 11. Emergence of Barley Seedlings When 200 kg/ha N were Applied Directly with Seed. Barley Plant Emergences were Recorded as Plants Present in 2.4 meters of Row.

Treatment	Dunstable site	Rich Valley site
Check	*129a	89a
$(NH_4)_2SO_4$	17b	58b
Urea	16b	5c
Coal humate-urea blend (ASHA 8B)	13b	4c
Coal humate + urea (ASHA 6B)	17b	6c
	**$S\bar{x}$=4.4	$S\bar{x}$=4.8

* In column values not followed by the same letter are significantly different at the 95% level of probability.
** Standard error of the mean.

greatly reduced by all nitrogen fertilizers (Table 11). Coal humate plus urea, coal humate-urea blend, and urea reduced emergence to about 10% of the control. At the Rich Valley site significantly better germination occurred with the ammonium sulphate treatment than with the other fertilizers. This site was not as dry as the Dunstable site, as it received irrigation one week after seeding. Increased moisture may have resulted in rapid hydrolysis of urea and a high soil pH in the area adjacent to the seeds.

These results indicate a mixture of urea and coal humate were as harmful to seedlings as urea alone when such materials were placed directly with the seed. The results showed that with respect to barley emergence there was no difference between the urea blend with ASHA and the mixture of urea and ASHA. This suggests the urea blend with ASHA may be chiefly a physical mixture. The slightly increased emergence from ammonium sulphate in

comparison to urea is in agreement with Allison (1966).

Greenhouse Experiments

Nitrogen and Sulphur Supplying Power of Ammoniated Sulfomethylated Coal Humic Acid

Information was desired about two characteristics of ASHA: the ability to supply nitrogen to plants and the ability to supply sulphur to plants. A randomized complete block experiment was designed to test these two characteristics. It consisted of two subsections, one dealing with nitrogen and the other with sulphur. Barley was grown in the greenhouse on a Grey Luvisol soil which was deficient in both nitrogen and sulphur.

The treatments numbered 1 to 5 (Table 12) were designed to test if ASHA, when applied at low rates, provided plant growth stimulation and greater nitrogen and sulphur utilization efficiency by plants. The results showed large plant growth responses in relation to the level of nitrogen applied (Table 12). There was no greater plant growth on the pots receiving an organic nitrogen source as compared to the pots receiving an inorganic nitrogen source. The nitrogen uptake efficiency by the plants was about the same for both sources of nitrogen.

These results are in contradiction to those of Khristeva (1963). Khristeva found that coal humates increased the efficiency of uptake of nutrients when the humates were applied at low rates and stress for available nutrients occurred. She also obtained growth stimulation from the coal humates when they were applied at low rates.

Sulphur, applied either as Na_2SO_4 or ASHA, greatly increased plant growth and sulphur uptake. The increases were slightly larger

Table 12. Barley Dry Matter and N and S Yields for Greenhouse Pot Experiments.

Treatment	Total dry matter g/pot	N yield g/pot	Net % recovery of added N	% S in dry matter	Ratio N/S in dry matter	S yield g/pot	Net % recovery of added S
(1) PKS	*2.28f	0.044f					
(2) N15PKS	3.11cd	0.062e	84				
(3) N30PKS	3.36c	0.078d	78				
(4) ASHA(N15)PKS	2.87de	0.063e	86				
(5) ASHA(N30)PKS	3.35c	0.081d	85				
(6) NPKS	4.29a	0.126b	70	0.36	9.1	0.0139a	31
(7) NPK (S from ASHA)	3.84b	0.145a	62	0.30	12.5	0.0117b	25
(8) NPK	2.58e	0.093c	49	0.09	40.6	0.0023c	
	**$S_{\bar{x}}$=0.119	$S_{\bar{x}}$=0.00229					

* In column values not followed by the same letter are significantly different at the 95% level of probability.

** Standard error of the mean.

with Na_2SO_4 than ASHA (Table 12). The control treatment (Treatment 8, table 12) showed an N/S ratio of 40.6 which indicated a marked sulphur deficiency. The Na_2SO_4 and ASHA treatments gave N/S ratios of 9.1 and 12.5 which indicated adequate sulphur nutrition (Stewart and Whitehead, 1965). The N/S ratio and the S yield of the barley which was fertilized with ASHA indicated that the sulfomethyl sulphur contained in the ASHA was available to barley. Because of the small amount of sulphur taken up by the plants it was not determined if the ASHA and the Na_2SO_4 differed greatly in efficiency of supplying sulphur.

Ability of Coal Humic Acids to Alleviate Soil Acidity Damage to Crops

Pot Experiment with Barley Grown on an Acid Soil

This experiment was designed to test if growth of barley could be improved by additions of coal humates to an acid soil where soluble aluminum was known to be a major factor limiting plant growth. Husky barley was grown because it is very sensitive to aluminum toxicity and therefore would serve as an indicator of soluble aluminum (Hoyt and Nyborg, 1970).

The pots treated with calcium humate gave three times larger barley yields than the pots which were treated with sufficient $Ca(OH)_2$ to give about the same soil pH (Table 13). The soil pH after harvest of the above two treatments was 4.72 and 4.64 respectively. This difference in soil pH was not large enough to account for the difference in barley growth. These results agreed with Hoyt (1970) who found that organic materials reduced soil acidity damage on acid soils. The cal-

Table 13. Yield of Barley Grown on Acid Soil, soil pH, and Soluble Aluminum and Manganese.

Treatment	Barley yield dry matter g/pot	Soil pH after harvest	$CaCl_2$ soluble after harvest Al ppm	Mn ppm
Check	*0.62c	4.49	29.6	3.1
$Ca(OH)_2$ to neutralize soil	8.83a	7.15	0.4	0.0
Ca humate	2.94b	4.72	16.5	3.3
NH_4 humate(PHSC 10B)	0.35c	4.48	26.0	4.5
$Ca(OH)_2$ to give equivalent pH as Ca humate treatment	0.99c	4.64	23.0	2.7
	$**S\bar{x}=0.28$			

* In column values not followed by the same letter are significantly different at the 95% level of probability.
** Standard error of the mean.

cium humate treated soil had 16.5 ppm soluble aluminum as compared to 23.0 ppm soluble aluminum on the $Ca(OH)_2$ (Table 13). These results suggest that reduction of soluble soil aluminum may be the cause of the increased growth.

The reduction of yields on the NH_4 humate plots as compared to the untreated soil were not significant, but this is partly because of the lack of sensitivity of Duncan's Multiple Range when such a wide range of treatment occurs. The reduction in barley yield seems to be real. This reduction is in agreement with the work of Nyborg (1970) who showed when barley grown on this soil was supplied with a nitrate nitrogen source, yields were three times those when it was supplied with an ammonium nitrogen source. Reasons for the above reduction in

yields were not established.

Pot Experiment with Alfalfa Grown on Acid Soils

This experiment was designed to test if coal humates had any ability to reduce damage to plants caused by soluble aluminum in acid soils. Alfalfa was grown on three acid soils, which had different levels of soluble aluminum. Treatments of calcium humate and $Ca(OH)_2$ were applied to each soil. The rate of application of the calcium hydroxide was estimated to bring the soil to the same pH as the calcium humate treatment.

In the soils which had high amounts of soluble aluminum the results showed increases in growth of alfalfa on the pots treated with calcium humate over the growth on the pots treated with $Ca(OH)_2$ (Table 14). The Josephine loam and the Alcan silt loam showed highly toxic and moderately toxic amounts of soluble aluminum respectively in the soil after the harvest (Table 14). On both these soils calcium humate treatments showed significantly increased growth of alfalfa over the growth on the $Ca(OH)_2$ treated soil. The Alcan clay loam soil had 0.6 ppm of soluble aluminum which was not sufficient to interfere with the alfalfa growth. On this soil the yield of alfalfa was higher on the pots treated with $Ca(OH)_2$. The reason for this increase in growth may be the higher pH of the pots treated with $Ca(OH)_2$. This higher pH and more readily available Ca in the $Ca(OH)_2$ pots may have caused increased nitrogen fixation by favorable conditions for *Rhizobium* nodulation. Examination of the alfalfa roots from the soils treated with $Ca(OH)_2$ and the soils treated with Ca humate showed slightly more and healthier nodules present in the former soil.

Table 14. Yields of Alfalfa Grown on Ca Humate and $Ca(OH)_2$ Treated Acid Soils and After Harvest Soil pH, Soluble Al and Soluble Mn.

Soil	Treatment	Alfalfa dry matter yields g/pot	Soil pH after harvest	$CaCl_2$ soluble after harvest	
				Al ppm	Mn ppm
Josephine loam	Ca humate	*0.50e	4.32	19.0	4.4
	$Ca(OH)_2$	0.09f	4.42	23.0	2.7
Alcan silt loam	Ca humate	1.30c	5.10	5.0	3.4
	$Ca(OH)_2$	0.95d	5.16	6.0	2.7
Alcan clay loam	Ca humate	2.03b	5.64	0.6	2.9
	$Ca(OH)_2$	2.46a	5.98	0.6	2.0
		**$S\bar{x}$=0.073			

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.
** Standard error of the mean.

In the Josephine and Alcan silt loam soils Ca humate treatments resulted in slightly lower soil pH than $Ca(OH)_2$ treatments (Table 14). However, despite the lower pH, Ca humate treatments showed less soluble Al. This was accompanied by more soluble manganese in the soil with the humate treatments. However, the growth of Husky barley is not impaired by soluble manganese until the manganese concentration is greater than 20 ppm (Hoyt and Nyborg, 1970). The reasons for these differences in levels of soluble aluminum and soluble manganese were not established. The alfalfa growth was increased by a calcium humate treatment on those soils which had a large amount of soluble aluminum. The calcium humates reduced the soluble aluminum on the soils where it gave a good growth effect on alfalfa. This suggests the increased alfalfa growth was due to reduction of soluble aluminum.

Structural Effects of Organic Amendments to Soil

Experiments were conducted to determine if coal humates could be used to improve structure on certain poorly structured Solonetzic and Luvisolic soils. Coal humates are believed to have a structure similar to soil humic acids, which play a major role in soil aggregation and structure formation. However, sulfomethylated coal humates act as a dispersing agent and have low wettability. Such characteristics could have quite an unfavorable effect on structure.

Aggregate Analysis Experiments

Water stable aggregation is an important characteristic of agricultural soils. Many Solonetzic soils form hard aggregates when dry, but when wet such aggregates slake, forming a soil which has low hydraulic conductivity.

The effect on soil aggregation of coal humates and two lignin products was measured with three Solonetzic soils. Coal humates, applied at a rate of 2.0% by weight, did significantly increase aggregation as contrasted to the control on the Nampa clay loam and gave slight increases on the other two soils (Table 15). Coal humates, applied at a rate of 0.2%, did not give significant increases in aggregation on any of the soils. The ammoniated form of lignin, when applied at the 2.0% rate, gave pronounced increases in aggregation on all three soils, as contrasted to the control, but when applied at the 0.2% rate, it did not significantly influence aggregation. The sodium form of lignin was tried only on the Nampa soil. Increases in soil aggregation from the sodium form of lignin were not as large as with the ammonium form of lignin.

Table 15. Aggregate Analysis Mean Weight Diameters (MWD) of Aggregates for Three Soils Receiving Various Structural Treatments.

Treatment	Duagh silty clay loam MWD in mm	Nampa clay loam MWD in mm	Black Solod loam MWD in mm
Check	*0.061b	0.033d	0.026b
ASHA - 2.0%	0.083b	0.173c	0.031b
ASHA - 0.2%	0.103b	0.074d	0.024b
Orzan A - 2.0%	0.479a	0.580a	0.471a
Orzan A - 0.2%	0.098b	0.075d	0.032b
Orzan S - 2.0%	_	0.324b	_
Orzan S - 0.2%	_	0.029d	_
	**$S\bar{x}$=0.023	$S\bar{x}$=0.027	$S\bar{x}$=0.063

* In column values not followed by the same letter are significantly different at the 95% level of probability.
** Standard error of the mean.

The behaviour of the coal humates, as determined in this experiment, may not apply under different experimental conditions or procedures. The method used consisted of drying preformed aggregates and then wetting the aggregates for ten minutes prior to shaking. The coal humates displayed a tendency to migrate to the soil surface when drying occurred, and therefore the increased aggregation caused by the coal humates may be the result of a surface layer of coal humate material reducing the wettability of the aggregates. However, the Orzan treated soil showed no evidence of surface layers of Orzan materials, so similar aggregation should occur if a moist sample were analyzed.

The soil aggregation was also measured on samples taken ten weeks after harvest on the ammonium sulphate and coal humate plots from the

Table 16. Aggregate Analysis Mean Weight Diameters (MWD) of Aggregates for Soil from Rich Valley Field Fertilizer Plots, Ten Weeks After Harvest.

Treatment	MWD in mm
$(NH_4)_2SO_4$ at 480 kg/ha	*0.070a
Coal humate (PHSC 10B) at 2482 kg/ha	0.101a
	**$S\bar{x}$=0.0162

* In column values not followed by the same letter are significantly different at the 95% level of probability.
** Standard error of the mean.

Rich Valley field fertilizer experiment. A slight increase in aggregation was present on the plots receiving coal humates as contrasted to the ammonium sulphate plots (Table 16). After the growing season the exchangeable ammonium content of the soil was quite low (Table 2) and consequently the humates were present in a form other than the water-soluble ammonium humate. In addition, coatings of coal humates no longer appeared when the soil surface dried, further indicating that the humates were no longer present in the water-soluble ammonium form. It therefore appears the aggregation effect of the ammonium form of coal humate persists even after its form is altered.

The results reported here show small increases in aggregation with coal humates and large increases in aggregation from the ammonium form of lignin. Gussak (1961) applied treatments of coal and lignin to Sierozems and in both cases found little improvement in soil aggregation. Webber (1959) and Doyle and MacLean (1959) found that lignin products increased soil aggregation, but disagreed regarding the permanency of this increased aggregation.

Soil Crusting Experiments

Poorly structured soils frequently slake when wet and then form a hard surface crust when dry. The Duagh Black Solonetz, Nampa Grey Solod, and the Black Solod from Stettler all exhibited unfavorable crusting characteristics in the field. Measurements of crusting were carried out with a pocket penetrometer on the above soils on the same samples which had been prepared for aggregate analysis. The results from penetrometer readings (Table 17) were not precise enough to indicate if coal humates altered the soil crust strength. The Black Solod showed increased crusting in the dishes which had received coal humate treatments, but this was caused by a coal humate layer that accumulated on the soil surface with drying of the soil. The ammonium salt of lignin slightly increased crusting readings and the sodium salt of lignin increased soil crust strengths greatly. No information could be obtained from the

---

Table 17. Penetrometer Readings of Soil Crusting as kg/sq cm.

Treatment	Duagh silty clay loam	Nampa clay loam	Black Solod loam
Check	*4.5+	3.8	1.0
Coal humate (PHSC 10B) - 2.0%	4.5+	3.0	2.0
Coal humate (PHSC 10B) - 0.2%	4.5+	3.2	1.4
NH_4 lignin (Orzan A) - 2.0%	4.5+	4.3	2.1
NH_4 lignin (Orzan A) - 0.2%	4.5+	3.3	1.2
Na lignin (Orzan S) - 2.0%	_	4.5+	_
Na lignin (Orzan S) - 0.2%	_	4.5+	_

* Readings of crusting went off scale of penetrometer.

Duagh soil as crust breaking strengths were too large to show on the penetrometer scale.

The pocket penetrometer gives only very approximate data on soil crusting. The standard method of measuring crust strength, Modulus of Rupture (Reeve, 1965), did not prove satisfactory because the coal humate treated soils formed curved briquets.

Hydraulic Conductivity Experiment

Agricultural use of many soils is restricted by limited water movement within the profile. One of the methods of measuring a soil's internal drainage characteristics is hydraulic conductivity.

Hydraulic conductivities were determined on disturbed soil samples of Nampa clay loam (a Grey Solod) and loam from a Black Solod after 48 hours flow of deionized water. These soils received additions of ammonium chloride and calcium chloride, ammonium and calcium forms of sulfomethylated coal humates, ammonium and calcium forms of lignin, and an ammonium form of rusty coal (leonardite).

Ammonium chloride and calcium chloride were used to determine the effect of NH_4 and Ca ions on hydraulic conductivity. The results (Table 18) showed that these ions both significantly increased hydraulic conductivities. Initially the NH_4 coal humates decreased the hydraulic conductivity. However, the NH_4 and Ca forms of sulfomethylated coal humates had similar hydraulic conductivities as the control when conductivity was measured after 48 hours. The NH_4 form of rusty coal (PHSC 6A) reduced hydraulic conductivities on both soils. The difference in rates of flow between the rusty coal and the control was greatest at the commencement of water flow, because the hydraulic conductivity of the con-

Table 18. Hydraulic Conductivity of Soils as Influenced by NH_4 and Ca Salts, Ammonium and Calcium Forms of Sulfomethylated Coal Humic Acids and Lignisol, and Ammoniated Rusty Coal.

Treatment	Nampa Series, Ap hydraulic conductivity, cm/hr	Black Solod, Ap hydraulic conductivity, cm/hr
Check	*0.041c	0.144d
0.11% NH_4Cl	0.131ab	0.262c
0.22% $CaCl_2$	0.185a	0.400b
1.0% NH_4 coal humate (PHSC 10B)	0.040c	0.149d
1.0% Ca coal humate	0.041c	0.147d
1.0% NH_4 lignin (Lignisol TSD)	0.109b	0.389b
1.0% Ca lignin (Lignisol BD)	0.104b	0.484a
1.0% NH_4 rusty coal	0.015c	0.083e
	**$S\bar{x}$=0.0168	$S\bar{x}$=0.0138

* Values not followed by the same letter in a column are significantly different at the 95% level of probability.
** Standard error of the mean.

trol declined considerably with time. Ca and NH_4 forms of lignin gave increased flow rates as compared to the control. Also the rates of hydraulic conductivity did not decline as much during 48 hours in the lignin treated columns as in the control.

It was also noted that when the dry columns were immersed in a beaker of deionized water, the rates of advance of the wetting front in the soils treated with NH_4 coal humates and rusty coal were about 40% of the rate in the other soils.

The results of the hydraulic conductivity experiment and rate of wetting observation show that the NH_4 form of sulfomethylated coal humate

initially restricts wetting and rate of water movement in soil, but later the coal humate treated soil has a hydraulic conductivity similar to untreated soil. The soils treated with the Ca form of humate behaved similar to untreated soils. Applications of Ca and NH_4 forms of lignin to soil increased hydraulic conductivity. Calcium or ammonium ions appear to be as effective a method and a simpler method of increasing hydraulic conductivity as organic compounds. Rusty coal may have some value for engineering purposes where reduced hydraulic conductivity of soils is desired.

The results (Table 18) suggest that treatments of calcium are just as good as, if not better than, treatments of ammonium for increasing water movemement in Solonetzic soils. Van Schaik and Cairns (1969) stress the use of ammonium to increase soil permeability and they report that ammonium on Solonetzic soils increased the permeabilities to 50 times that of the control.

CONCLUSIONS

A number of conclusions, based on this study and on the available literature, are presented regarding the agricultural use of ammoniated sulfomethylated humic acids (ASHA). In addition, several conclusions pertaining to other aspects of soil science are drawn from results of this study.

1. It was shown that ASHA did not function to any appreciable degree as a slow-release nitrogen fertilizer. The exchangeable ammonium in the ASHA was made available to plants at about the same rate as the nitrogen in ammonium sulphate, sodium nitrate, and urea. Very little of the bound nitrogen contained within the ASHA was released during one growing season. Similarly, a blend of ASHA and urea did not show slow release of its nitrogen. On three out of four field sites sodium nitrate fertilizer proved to be more efficient than ammonium sulphate and urea in supplying nitrogen to barley and perennial grass.

2. ASHA, which contains added sulfomethyl sulphur, was shown to supply at least part of that sulphur to barley.

3. When mixed with acid soils which contained toxic levels of soluble aluminum, ASHA was found to improve plant growth.

The benefits of humates on acid soils seemed to be related to chelation or fixation of soluble aluminum in the soil, thus reducing the amount of soluble aluminum ions and the harmful effect of aluminum ions on plants. The economic value of this effect remains in doubt as toxic levels of soluble aluminum can be eliminated by additions of lime.

4. Plants fertilized with ASHA did not show special growth ben-

efits or efficiency of utilization of fertilizers other than the improved growth previously mentioned on soils high in soluble aluminum. No evidence was found to support claims that coal humates increased fertilizer efficiencies, reduced toxicity effects of excess fertilizers, or acted as stimulants to plant growth.

It has frequently been reported in soils literature that humic additives to soil have special growth benefits to plants, other than supplying necessary chemical nutrients. A number of reasons were stated in the literature for such growth benefits. The consensus of opinion of recent workers was that when such plant growth benefits occurred with plants grown in nutrient solutions, they were related to chelation of iron by the humates and growth benefits to plants did not occur where conditions for adequate iron supply existed. However, insufficient iron supply for plant growth does not often appear to be a problem when plants are grown in soil. Khristeva (1963) reported positive plant growth on Podzols and Sod Podzols when they were fertilized with organic fertilizers, as contrasted to chemical fertilizers. However, she did not associate such increased plant growth with reduction of toxic levels of aluminum.

5. Soil structure work showed that ASHA increased the stability of soil aggregates in water. The effect of ASHA on crusting of soils was inconclusive. Calcium and ammonium forms of sulfomethylated coal humates did not alter the hydraulic conductivity of soil. The ammonium salt of rusty coal greatly reduced the hydraulic conductivity of soils, and perhaps there are possibilities for practical use of this material where low water intake by soils is desired. Ammonium and calcium forms

of lignin wastes from the bisulphite paper manufacturing process were found to improve soil structure. However, calcium chloride and ammonium chloride were found to be equally as effective in improving the hydraulic conductivity of Solonetzic soils as organic salts of calcium and ammonium.

REFERENCES CITED

ALDERFER, R. B. and SHARP, W. C. 1955. Effect of clarion extract on the physical and chemical characteristics of the soil. Penn. State Univ. Progress Report 133. From Studies with waste sulphite liquor. 1959. J. Doyle and A. MacLean. Can. J. Soil Sci. 39: 87-97.

ALEXANDER, M. 1961. Introduction to soil microbiology. John Wiley & Sons, New York.

ALLISON, F. E. 1965. Evaluation of incoming and outgoing processes that affect soil nitrogen. In Soil nitrogen. W. V. Bartholomew and F. E. Clark, Eds. Amer. Soc. Agron. Madison, Wisconsin. 573-606.

ALLISON, F. E. 1966. The fate of nitrogen applied to soils. In Advan. Agron. Academic Press, New York. 219-259.

ASO, S. and SAKAI, I. 1963. Studies on the physiological effects of humic acid. Soil Sci. and Plant Nutrition. 3: 85-91.

ASO, S. and TAKENAGA, H. 1968. Studies on the physiological effects of humic acid. Soil Sci. and Plant Nutrition. No. 6. 14: 231-237.

BEATON, J. D., HUBBARD, W. A. and SPEER, R. C. 1967. Coated urea, thiourea, urea-formaldehyde, hexamine, oxamide, glycoluril, and oxidized nitrogen-enriched coal as slowly available sources of nitrogen for orchardgrass. Agron. Journal. No. 2. 59: 127-133.

BENTLEY, C. F. 1956. Equipment for seeding fertilizer experiments with small grains. Can. J. Agr. Sci. No. 6. 36: 508-509.

BERKOWITZ, N., MOSCHOPEDIS, S. E. and WOOD, J. C. 1963. On the structure of humic acids. Paper presented by Moschopedis at the 143 Nat. Meeting of Amer. Chem. Soc. Fuel Section.

BOWSER, W. E., KJEARSGAARD, A. A., PETERS, T.W. and WELLS, R. E. 1962. Soil survey of the Edmonton sheet (83-H). Canada Dept. of Agr.

BREMNER, J. M. 1965. Inorganic forms of nitrogen, exchangeable ammonium, nitrate, and nitrite by steam distillation methods. In Methods of soil analysis. C. A. Black, Ed. Amer. Soc. Agron. Madison, Wisconsin. Part 2: 1191-1198.

CHAMINADE, R. 1958. Influence de la matière organique humifiée sur l'efficacité de l'azote. Ann. Agron. Paris. Ser. A. 9: 167-192.

DAVIDSON, D. T. 1965. Penetrometer measurements. In Methods of soil analysis. Agronomy No. 9, Part 1: 472-484. C. A. Black, Ed. Amer. Soc. Agron. Madison, Wisconsin.

DAWSON, M. D. 1958. Influence of base saturation and calcium levels on yield and mineral content of alfalfa. Soil Sci. Amer. Proc. 22: 328-333.

DEAN, G. A. 1966. A simple colorometric finish for the Johnson-Nishita microdistillation of sulphur in the soil. Analyst 91 (1085). 530-532.

DE KOCK, P. C. 1955. Influence of humic acids on plant growth. Sci. 121: 473.

DE KOCK, P. C. 1960. The effect of natural and synthetic chelating substances on the mineral status of plants. Trans. 7th Int. Congr. Soil Sci. Madison, Wisconsin. 3: 573.

DE KOCK, P. C. and STREMECKI, E. L. 1954. Growth promoting effects of a lignite. Physiol. Plantarum. 7: 504-512.

DOYLE, J. J. and MACLEAN, A. A. 1959. Studies with waste sulphite liquor. Can. J. Soil Sci. Aug.: 87-97.

DRAGUNOV, S. S. 1963. Peat humic fertilizers. Second Int. Peat Congr. Leningrad. Trans. II: 563-578.

FARSTAD, L., LORD, T. M., GREEN, A. J. and HORTIE, H. J. 1965. Soil survey of the Peace River area in British Columbia. Report No. 8 of the British Columbia Soil Survey. Queen's Printer, Ottawa.

FLAIG, W. 1963. Effect of humic substances on plant metabolism. Second Int. Peat Congr. Leningrad. Trans. II: 579-606.

FLAIG, W. 1968. Origin of nitrogen in coals. Chemical Geology. 3: 161-187.

FREEMAN, P. G. and FOWKES, W. W. 1969. Coal-derived humus plant growth effects. U. S. Dept. of the Interior. Bureau of Mines. Report No. 7203.

FUHR, F. and SAUERBECK, D. 1963. The uptake of straw decomposition products by plant roots. In Symp. The use of isotopes in soil organic matter studies. FAO/IAEA Brunswick-Vokenrode. Pergamon Press, Oxford. 73-84.

FUHR, F. and SAUERBECK, D. 1965. The spatial and chemical distribution of organic decomposition products taken up by the roots of Daucus carota. Sonderh. Landw. Forsch. In Bibl. 1182. Commonwealth Bur. of Soils. Harpenden, England. 12: 153-165.

GERASIMOV, I. P. 1962. Problems of Soviet Soil Science in the light of the new program and resolutions of the XXII Congress of the Soviet Union. Sov. Soil Sci. 1221-1230.

GREENLAND, D. J. 1965. Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds. Soils and Fertilizers. 28: 415-425.

GUMINSKI, S. 1968. Present day views on physiological effects induced in plant organisms by humic compounds. Sov. Soil Sci. II: 1250-1256.

GUSSAK, V. E. 1961. Application of humic acid and polymer preparations to Sierozems for the improvement of soil structure and erosion control. Sov. Soil Sci.

HAKEN, D. 1963. Utilization of composts containing peat and pig manure. Second Int. Peat Congr. Leningrad. Trans. II: 649-656.

HALL, A. D. 1905. The book of the Rothamstead experiments. E. P. Dutton and Co., New York.

HARMSEN, G. W. and KOLENBRANDER, G. J. 1965. Soil inorganic nitrogen. In Soil nitrogen. W. V. Bartholomew and F. E. Clark, Eds. Amer. Soc. Agron. Madison, Wisconsin. 43-92.

HEINRICH, G. 1964. Huminsäure und Permeabilität. Protoplasma. 58: 402-425.

HOYT, P. B. 1968. Report of the Alberta Soils Advisory Committee. 1965, 1966, 1967, 1968. Mimeograph.

HOYT, P. B. 1970. Unpublished data.

HOYT, P. B. and NYBORG, M. 1970. Unpublished data on aluminum and manganese toxicity. Personal communication.

JACKS, C. V. 1963. The biological nature of soil productivity. Soils and Fertilizers. 26: 147-150.

JOHNSON, C. M. and ULRICH, A. 1959. Total sulphur by nitric/perchloric acid. Analytical methods for use in plant analysis. Calif. Agric. Experimental Station. Bulletin no. 766. From Determination of sulphur in soils and plant material. Tech. Bull. No. 14. Sulphur Institute. Washington, D. C.

KANEDA, T. and MOSCHOPEDIS, S. 1969. Unpublished data. Alberta Research council, Edmonton.

KEMPER, W. O. and CHEPIL, W. S. 1965. Size distribution of aggregates. In Methods of soil analysis. Agronomy No. 9, Part I: 499-510. C. A. Black, Ed. Amer. Soc. Agron. Madison, Wisconsin.

KHRISTEVA, L. A. 1963. Theory of humic fertilizers and their practical use in the Ukraine. Second Int. Peat Congr. Leningrad. Trans. II: 543-558.

KHRISTEVA, L. A. and LUK'YANEKO, N. V. 1962. Role of physiologically active substances in the soil·humic acids, bitumens and vitamins B, C, P-P, A and D in the life of plants and their replenishment. Sov. Soil Sci. 1137-1141.

KONONOVA, M. M. and D'YKONOVA, K. V. 1960. Soil organic matter and plant nutrition. Sov. Soil Sci. 29-236.

KOZHEKOV, D. Z. H., LAZAREVA, M. M., ABASOVA, L. P., KULIKOVA, V. V. and KOVALEVA, YE. I. 1968. Influence of coal humic fertilizers on the yield of corn and sugar beets on Sierozemic soils. Sov. Soil Sci. II: 1128-1137.

MOSCHOPEDIS, S. E. 1965. Sulfomethylation of humic acids and coal. Canadian Patent no. 722,720. Granted to Canadian Patents and Developments, Limited, Ottawa.

MOSCHOPEDIS, S. E. 1967. Sulfomethylation of humic acids, lignites, and coals and products thereof. USA Patent no. 3,352,902. United States Patent Office.

MOSCHOPEDIS, S. E. 1970. Structure of coal humic acids. Personal communication.

NIKLEWSKI, M. 1963. Research on the agricultural utilization of peat in Poland. Second Int. Peat Congr. Leningrad. Trans. II: 705-720.

NYBORG, M. 1968. Sulphur deficiency in cereal grains. Can. J. Soil Sci. No. 1, Vol. 48: 37-41.

NYBORG, M. 1970. Unpublished data on barley growth responses to ammonium and nitrate nitrogen sources when grown on Josephine soil. Personal communication.

NYBORG, M. and HENNIG, A. M. F. 1969. Field experiments with different placements of fertilizers for barley, flax and rapeseed. Can. J. Soil Sci. 49: 79-88.

PARR, J. F. 1967. Biochemical considerations for increasing the efficiency of nitrogen fertilizers. Soils and Fertilizers. 30: 207-213.

PRAT, S. 1963 (a). Effect of humic substances on plants. Second Int. Peat Congr. Leningrad. Trans. II: 537-542.

PRAT, S. 1963 (b). Permeability and the effect of humic substances on plant cells. Second Int. Peat Congr. Leningrad. Trans. II: 607-610.

PRINCE, A. L. 1945. Determination of total nitrogen, ammonia, nitrates and nitrites in the soil. Soil Sci. 59: 47-52.

REEDER, S. W. and ODYNSKY, W. 1965. Soil survey of the Cherry Point and Hines Creek area. University of Alberta Bulletin. University of Alberta, Edmonton. 55-56.

REEVE, R. C. 1965. Modulus of Rupture. In Methods of soil analysis. Agronomy No. 9, Part 1: 466-471. C. A. Black, Ed. Amer. Soc. Agron. Madison, Wisconsin.

RENNIE, D. A., TRUOG, E. and ALLEN, O. N. 1954. Soil aggregation as influenced by microbial gums, level of fertility and kind of crop. Soil Sci. Soc. Amer. Proc. 399-403.

ŘEŘÁBEK, J. 1963. The effect of humic acids on the growth and metabolism of plant cells. Advancing Frontiers in Plant Science. 6: 87-111.

RUSSELL, E. W. 1961. Soil conditions and plant growth. Longmanns, 9th ed. London.

RUSSELL, E. W. 1966. The role of organic matter in soil productivity. In The use of isotopes in soil organic matter studies. Symp. Pergamon Press, Oxford. 3-20.

SCHNITZER, M. and POAPST, P. A. 1967. Effects of a soil humic compound on root initiation. Nature. 213: 598-599.

SMIDOVA, M. 1962. Über den Einfluss von Na-Humat auf die Oxydations-Reduktions-Prozesse in den Wurzeln von Winterweizenpflanzen. Studies about Humus Symp. Pub. Czech. Acad. of Sciences. Prague. 291-304.

SOWDEN, F. J. and ATKINSON, H. J. 1951. The effect of waste sulphite liquor solids on the chemical and physical properties of soil. Sci. Agr. 31: 93-98.

STEWART, B. A. and WHITEHEAD, C. J. 1965. Effect of crop residues, soil temperatures and sulphur on growth of winter wheat. Soil Sci. Amer. Proc. 29: 752-755.

SUTER, C. M., BAIR, R. K. and BORDWELL, F. G. 1945. The sulfomethylation reactions. J. Organic Chemistry. 10: 470-478.

SWABY, R. J. 1950. Influence of humus on soil aggregation. J. Soil Sci. I: 182-194.

TOOGOOD, J. A. 1963. Youngstown irrigation experiments. Dept. of Soil Science. Edmonton.

US Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soil. US Dept. Agr. Handbook 60. L. A. Richards, Ed.

VAN BAVEL, C. 1950. Mean weight diameter of soil aggregates as a statistical index of aggregation. Soil Sci. Amer. Proc. 14: 20-23.

VAN SCHAIK, J. C. and CAIRNS, R. R. 1969. Salt and water movement in Solonetzic soils. Can. J. Soil Sci. 49: 205-210.

VIETS, F. G. 1965. The plants need for and use of nitrogen. In Soil nitrogen. W. V. Bartholomew and F. E. Clarke, Eds. Amer. Soc. Agron. Madison, Wisconsin.

WATT, G. W. and CHRISP, J. D. 1964. Spectophotometric method for determination of urea. Anal. Chem. 26: 452-453.

WEBBER, L. R. 1959. Note on the aggregate size distribution and aggregate stability in Haldimand clay treated with four soil additives. Can. J. Soil Sci. 39: 252-253.

WHITEHEAD, D. C. 1963. Some aspects of the influence of organic matter on soil fertility. Soils and Fertilizers. 26: 217-223.

APPENDIX I

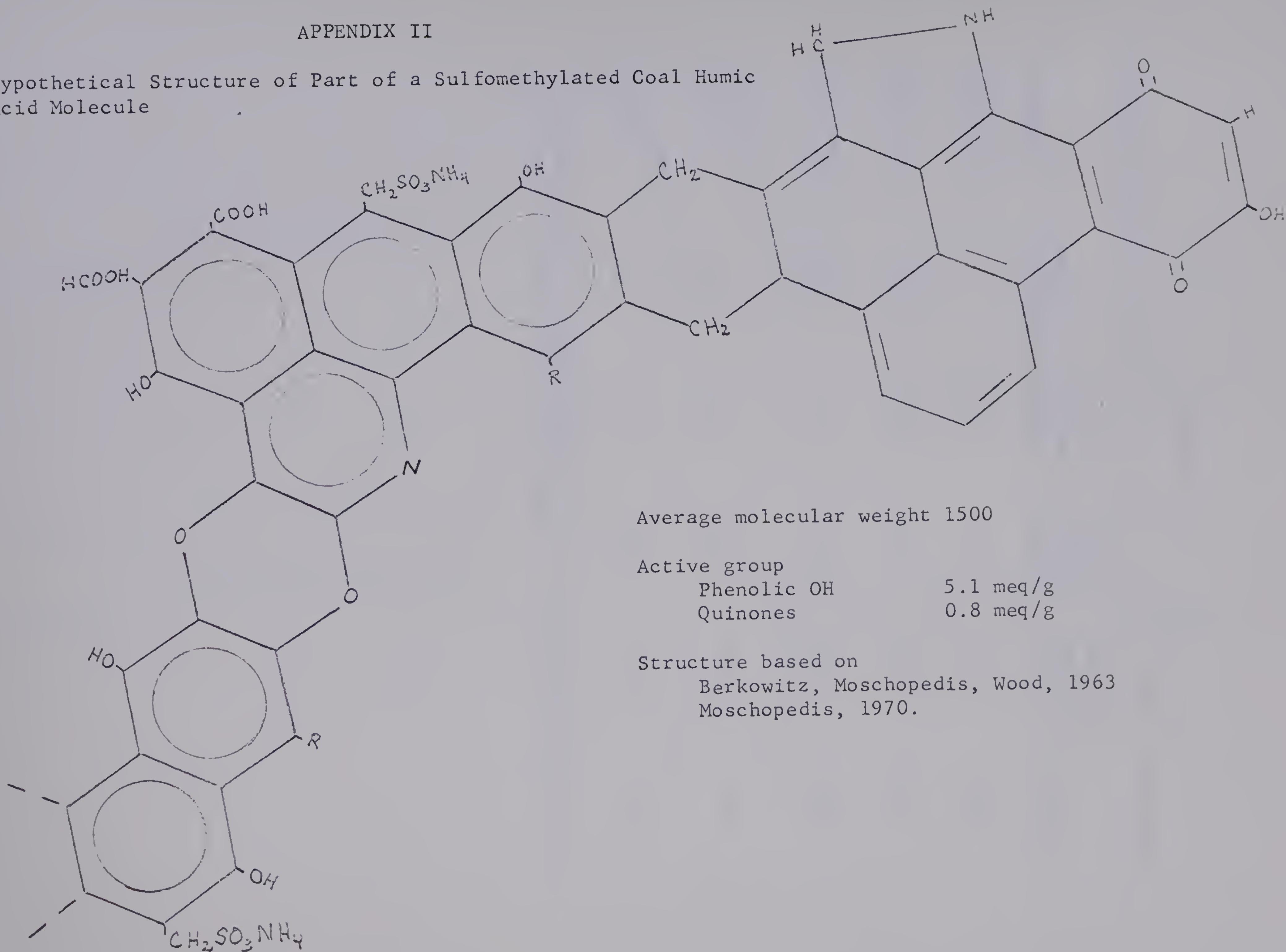
Coal Humic Fertilizers
Percent Composition on a Dry Weight Basis

	Rusty Coal II	NH_4 Rusty Coal PHSC 6A	*ASHA PHSC 6F	ASHA PHSC 8A (30% urea)	ASHA ***PHSC 6 Blend	ASHA PHSC 10 Blend	ASHA PHSC 8 Blend (30% urea)
Carbon	55.8	49.6	46.4	45.1	42.3	47.5	42.0
Hydrogen	3.1	2.9	3.2	3.4	3.1	3.2	4.1
Sulphur	0.5	0.5	1.9	1.7	2.3	2.2	1.8
**Nitrogen	1.7	4.6	5.9	14.0	5.4	4.8	14.3
Ash	12.6	18.8	21.1	15.5	20.8	19.3	15.0
Moisture		15.1			10.9	7.8	2.7

* Ammoniated sulfomethylated humic acids
** Determined by the Dumas Method.
Analytical data by the Alberta Research Council.
*** PHSC 6 Blend refers to the particular mixture made by the Alberta Research Council of several subsamples.

APPENDIX II

Hypothetical Structure of Part of a Sulfomethylated Coal Humic Acid Molecule



Average molecular weight 1500

Active group

Phenolic OH	5.1 meq/g
Quinones	0.8 meq/g

Structure based on

Berkowitz, Moschopedis, Wood, 1963

Moschopedis, 1970.

APPENDIX III

Nitrogen Analysis on Coal Humates Based on Moist Weight as Received

Treatment	Total N% Joolbauer	Total % N Dumas Method	Total % N Kjeldahl Method	Distill-able NH_4 + NO_3	Urea N
Coal humate PHSC 6F	–	* 5.9	5.2	3.0	0.0
Coal humate PHSC 6B	4.7	4.9	5.7	2.7	0.0
Coal humate PHSC 10B	4.9	4.5	5.1	2.7	0.0
Coal humate + urea PHSC 8A	–	14.0	13.2	2.5	6.6
Coal humate + urea PHSC 8B	14.1	13.9	13.3	2.5	8.3

* Calculated on dry weight basis.
Joolbauer and Dumas analyses performed by Alberta Research Council.

APPENDIX IV

Legal Land Locations and Soil Test Data of Field Sites

Rich Valley - (SE 25-56-3, W of 5) Grey Solonetz

	Available Nutrients, kg/ha								
Depth in cm	N	P	K	Na	pH	Conductivity mhos/cm^2	Organic Matter	Free Lime	Texture
0-15	3	13	184	High+	5.8	0.4	Med+	Nil	Med
15-30	1	0	175	High+	6.6	0.5	Low+	Low-	Med
30-45	1	0	210	High+	7.8	0.6	Low+	Low+	Med

Dunstable - (SW 12-57-2, W of 5) Gleyed Grey Luvisol

	Available Nutrients, kg/ha								
Depth in cm	N	P	K	Na	pH	Conductivity mhos/cm^2	Organic Matter	Free Lime	Texture
0-15	9	10	132	Med-	6.0	0.3	Low	Low-	Fine
15-30	3	15	271	Med+	6.1	0.4	Low	Low-	Fine
30-60	90+	3	258	High	7.4	0.7	Low	Med	Very Fine

APPENDIX IV (cont'd)

Busby - (SE 28-57-27, W of 4) Dark Grey Luvisol

	Available Nutrients, kg/ha					Conductivity			
Depth in cm	N	P	K	Na	pH	mhos/cm^2	Organic Matter	Free Lime	Texture
0-15	0	69	293	Low	5.9	0.3	Med-	Nil	Med
15-30	0	56	224	Low	6.4	0.3	Low+	Nil	Fine
30-60	0	24	245	Low+	6.5	0.3	Low+	Nil	Med
60-75	0	16	228	Low+	6.1	0.2	Low+	Nil	Med

Fort Saskatchewan Hospital Lawn

	Available Nutrients, kg/ha					Conductivity			
Depth in cm	N	P	K	Na	pH	mhos/cm^2	Organic Matter	Free Lime	Texture
0-15	0	54	267	Low	8.0	0.5	Med	Low	Med
15-30	0	25	197	Low	7.7	0.6	Med-	Low+	Coarse
30-60	4	11	188	Low	7.9	0.5	Low+	Low+	Coarse
60-75	21	0	123	Low	8.3	0.5	Low+	Med	Coarse

From the Edmonton Agricultural Soil and Feed Testing Lab Reports.
Samples collected May, 1969.

APPENDIX V

Rates of Application of Fertilizers in Field Plot Experiments

	Phosphorus, potassium and sulphur fertilizers applied to all treatments			Nitrogen Fertilizers				
	Triple super phosphate	KCl	Na_2SO_4	$(NH_4)_2SO_4$, $NaNO_3$ or urea	ASHA		ASHA + urea	
					Rate of fertilizer	Rate of extractable NH_4, NO_3	Rate of fertilizer	Rate of extractable NH_4, NO_3
Location	kg/ha of P_2O_5	kg/ha of K	kg/ha of S	kg/ha of N	kg/ha	kg/ha of N	kg/ha	kg/ha of N
Rich Valley	* 60.5	112.1	22.4	100.9	2482 PHSC 6F	74.5	950 PHSC 8A	86.7
Dunstable	* 60.5	112.1	22.4	100.9	3603 PHSC 6B	97.3	842 PHSC 8B	90.7
Busby	100.9	134.5	22.4	145.7	5208 PHSC 6B	140.6	1215 PHSC 8B	130.9
Fort Saskatchewan	100.9	134.5	22.4	168.1	6009 PHSC 6B	162.0	1402 PHSC 8B	151.0

* Drilled with seed.
Broadcast prior to seeding on barley plots, sites 1 and 2.
Broadcast on grass stands, sites 3 and 4.

APPENDIX VI

Greenhouse Experiments with Nitrogen and Sulphur Fertilizers

	Nutrients Applied			
Treatments	NH_4Cl solution mixed with soil	NH_4NO_3 solution mixed with soil	ASHA (PHSC 10B) powder mixed with soil	Na_2SO_4 solution mixed with soil
(1) PKS	–	–	–	25 ppm S
(2) N(15)PKS	15 ppm N	–	–	25 ppm S
(3) N(30)PKS	30 ppm N	–	–	25 ppm S
(4) Coal N(15)PKS	–	–	615 ppm coal 15 ppm N 12 ppm S	13 ppm S
(5) Coal N(30)PKS	–	–	1230 ppm coal 30 ppm N 25 ppm S	–
(6) NPKS	–	80 ppm N	–	25 ppm S
(7) NPK (S as coal)	–	80 ppm N	1250 ppm coal 25 ppm S 31 ppm N	–
(8) NPK	–	80 ppm N	–	–

All treatments received an application of KH_2PO_4 solution banded at 1 1/2 inches below the soil surface. This provided 20 ppm P and 25 ppm K.

APPENDIX VII

Greenhouse Pot Experiment with Sulfomethylated Coal Humic Acid Added to an Acid Soil (Josephine Series).

Treatment	$Ca(OH)_2$ mixed with dry soil	Ca humate mixed with dry soil	NH_4 humate mixed with dry soil
Check	–	–	–
$Ca(OH)_2$ to produce neutrality	to produce neutrality	–	–
Ca salt prepared from coal humate (PHSC 10B)	–	0.35% by weight	–
NH_4 salt of coal humate (PHSC 10B)	–	–	0.35% by by weight
$Ca(OH)_2$ to provide equivalent pH as the Ca salt	0.0052% by weight	–	–

All treatments received an application of KH_2PO_4 solution banded at 1 1/2 inches below the soil. This provided 20 ppm P and 25 ppm K. They also received an application of $Ca(NO_3)_2$ solution mixed with the soil to provide 120 ppm N.